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FINAL REPORT

THEORETICAL STUDIES RELATING TO THE STRUCTURE AND PROPERTIES OF LEAD AZIDES BEFORE AND AFTER ENERGY INTERACTIONS

Covering the period
9 October 1959 to 9 November 1960

Contract No. DA-44-009-ENG-4156

Department of the Army
Project Number 8-07-11-440

Report prepared for

U. S. Army Research and Development Laboratories
Corps of Engineers
Fort Belvoir, Virginia

Submitted by

P.E.C. CORPORATION
1001 Mapleton Avenue
Boulder, Colorado

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PREFACE

This is a final report submitted under Contract
DA-44-009-ENG-4158. This report supersedes all
quarterly reports submitted under this contract.

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SUMMARY

A probability theory is developed to describe the initiation of detonation.

A new solid state reaction rate theory is presented. Some preliminary applications are made to drop-height experiments.

Calculations are made to determine the theoretical dielectric constant and loss tangent of a dielectric medium containing impurities.

Conclusions and recommendations are presented at the end of each chapter.

MODEL FOR INITIATION

D. S. Ling, Jr.

Introduction

In a previous report[1] we considered a simplified model
of the initiation process. For brevity we will term this
the "single-point" model. In this report we continue the
development of this model.

Section I reviews briefly the basic ideas of the model.
In Section II the method of moments is applied to the fund-
amental differential equation of the model. Section III
shows how the saddle point method (method of steepest
descent) may be used to solve the moment equations. Section
IV presents an improved solution of the differential
equation. This improved solution is still based on the
method of moments but permits one to neglect higher moments
with much less error. The method of Section IV gives a
completely adequate solution of the differential equation
and thus constitutes a complete mathematical treatment of
the model. Section V shows how the model may be made more
realistic while still remaining a single-point model. The
methods of Section V have been used in the actual numerical

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1. First Quarterly Technical Report, Contract DA-44-009-
   ENG-4158, 9 October 1959 to 5 February 1960, prepared
   by P.E.C. Corporation.

calculations. Section VI discusses the important question of the actual probability of initiation of explosion as predicted by the "single-point" model. Section VII presents the results of some numerical calculations. Section VIII presents some concluding remarks and makes recommendations for future investigation.

Discussion

Section I. The "Single-Point" Model of Initiation.

The basic idea of the "single-point" model is to assume that conditions are uniform over the very small region of the explosive in which initiation occurs. Because reactions are occurring, the small region is at a higher temperature, T, than the temperature T_o of the surroundings. However, as was discussed in greater detail in the earlier report, rather than assign a definite temperature T to the small heated region, we introduce a probability function $P(T,t)$ for the region. Thus $P(T,t)dT$ is the probability that at time t the temperature of the region lies between T and $T+dT$. Very briefly stated, the reason for this approach is that when very small numbers of molecules are involved we cannot properly speak of the number of reactions which occur in a time interval but can only state the probability that a reaction occurs in said time interval. Thus at any time we can never really say how many reactions have occurred and therefore we cannot know how much the temperature of the region has been raised. Rather, we can only state the probability of a certain number of reactions and there-fore the probability that the temperature has a certain value.

The small region (the "single-point" since conditions are assumed to be uniform over the region) will lose heat to the surroundings by thermal conduction at a rate given

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by $K(T-T_0)$. The constant K can be related to the thermal conductivity, k, of the region (see earlier report) with the result

$$K = 2\pi N^{2/3} rk$$

    with N = number of molecules in the small region

        r = radius of the region

        k = thermal conductivity of the medium

N and r may, of course, be related by introducing the volume occupied by a single molecule. In Section V we will introduce a different expression for K. This will not, however, invalidate any of the development which follows in Sections I, II, III and IV.

Reactions are assumed to occur in the small region with a probability per unit time given by

$$p(T) = NAe^{-E/kT}$$

E is the activation energy and A is the frequency factor of the Arrhenius equation. N is the number of molecules in the region. k is Boltzmann's constant. It will be convenient to measure temperature in energy units, thus in all that follows T stands for k times the temperature. If we choose E itself as an energy unit and let $U = NA$ then we have the simpler expression

$$p(T) = Ue^{-1/T}$$

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If each reaction releases an amount of energy Q
we will assume this to be immediately distributed
uniformly over the entire region of the "single-point".
This is clearly a rather unrealistic assumption but it
is necessary in order to preserve the "single-point"
nature of the model. This energy, Q, will cause T to
increase by an amount "q". "q" is clearly related to
Q, N and C, the specific heat of the medium. The exact
expression is given in Section V.

We must now derive the equation satisified by
$P(T,t)$. That is, we must show how to get $P(T,t+dt)$
if we know $P(T,t)$. The following derivation is exactly
that presented in the earlier report but is developed
here in greater detail. What is the probability that at
time t+dt the temperature lies between T and T+ΔT? This
probabilty can clearly arise in two ways.

1) The temperature at time t may lie between T-q
   and (T-q)+ΔT. If now a reaction occurs in the
   time dt, the temperature will be increased by
   an amount q and thus at t+dt the temperature will
   lie between T and T+ΔT. The probability of this
   event is clearly given by

   $$[P(T-q,t)\Delta T][p(T-q)dt]$$

   The first bracket gives the probability of
   temperature between T-q and T-q+ΔT at the time t.

The second bracket gives the probability that
a reaction occurs in the time interval dt if
the temperature is T-q. The product of these
two probabilities gives the probability of
event (1).

2) The temperature at time t may be slightly
greater than T by just enough so that in the
time interval dt the heat conduction loss brings
the temperature down to T. Let T' be the
temperature at time t. Then if the temperature
changes by heat conduction alone, it is clear
that;

$$T = T'-K(T'-T_0)dt$$
$$\text{or } T'=(T-KT_0dt)(1-Kdt)^{-1}$$
$$=(T-KT_0dt)(1+Kdt)$$
$$= T+K(T-T_0)dt \tag{1}$$

Now no reaction is to occur in the time interval
dt and the probability of this is given by
$1-p(T')dt$. Since $p(T')$ is multiplied by dt and
is thus a first order small quantity, we may
replace its argument T' by T. Thus the probability
of no reaction is given by $1-p(T)dt$. This must
be multiplied by the probability that the temp-
erature is T' at the time t. This is given by

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$P(T,t)\Delta T$ This event (2) occurs with the probability

$$[1-p(T)dt]P(T',t)\Delta T'$$

We can now state that

$$P(T,t+dt)\Delta T = [1-p(T)dt]P(T',t)\Delta T'$$

$$+ [P(T-q,t)\Delta T][p(T-q)dt]$$

We now write

$$P(T,t+dt) = P(T,t) + \frac{\partial P}{\partial t}dt$$

and

$$P(T',t) = P(T+K(T-T_0)dt,t)$$

$$= P(T,t) + \frac{\partial P}{\partial T}K(T-T_0)dt$$

Also by differentiating the relation (1) between T' and T we see that

$$\Delta T' = (1+Kdt)\Delta T$$

Ie., heat conduction produces a compression of temperature intervals by the factor $\frac{1}{1+Kdt}$. This compression is easily seen in the large time limit. If the only changes occurring are due to heat conduction, then regardless of how broad a distribution, P(T), we begin with, in a very large time it must become a very narrow peak at the ambient temperature T_0.

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If we now make the above substitutions and cancel the common factor ΔT, we find

$$[P+ \frac{\partial P}{\partial t} dt] = [1-p(T)dt][P+ \frac{\partial P}{\partial T} K(T-T_0)dt][1+Kdt]$$

$$+P(T-q,t)p(T-q)dt$$

$$= P+dt[KP+K(T-T_0)\frac{\partial P}{\partial T} -pP]$$

$$+ \text{ terms in } (dt)^2 \text{ of higher.}$$

Thus

$$\frac{\partial P}{\partial t} = KP+K(T-T_0)\frac{\partial P}{\partial T} -p(T)P(T)+p(T-q)P(T-q) \qquad (2)$$

Except where indicated in the last term, the arguments of P are T and t. This equation is the basic differential equation of the model. The solution of this is considered in the next three sections.

The boundary condition on (2) is $\lim_{T \to \infty} P(T,t) = 0$. The initial distribution, $P(T,0)$, must be given and will usually be taken as $\delta(T-T_0-q)$ where δ is the Dirac delta function. This corresponds to a single reaction occurring at $t = 0$ thereby raising the temperature to T_0+q. The temperature of the "point" can never drop below the temperature T_0 of the surroundings. This imposes the condition $P(T,t) = 0$ for $T < T_0$.

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<u>Section II.</u> The Method of Moments.

In order to solve equation (2) we consider the
moments of $P(T)$ defined by

$$\bar{M}_n(t) = \int_{T_o}^{\infty} T^n P(T,t) \, dT$$

The zero moment, $\bar{M}_0(t) = \int_{T_o} P(T,t) \, dT$, is the probability
that the temperature of the "point" has some value and,
therefore, $\bar{M}_0(t) = 1$. The first moment gives the expecta-
tion (or mean) value of the temperature at the point. We
will frequently denote it by $\theta(t)$. Thus

$$\bar{M}_1(t) = \theta(t) = \int_{T_o}^{\infty} T P(T,t) \, dT \tag{3}$$

It will be most convenient to redefine the moments
and measure them relative to the mean temperature, θ.
This is a change from the earlier report. We define

$$M_n(t) = \int_{T_o}^{\infty} (T-\theta)^n P(T,t) \, dT \tag{4}$$

It is clear that $M_0(t) = 1$ but that now $M_1(t) = 0$. The
mean square deviation, $M_2(t)$, will be commonly denoted
by $\Delta(t)$.

The moment equations are now obtained by multiplying
(2) by $(T-\theta)^n$ and integrating from T_o to ∞. We will
treat in turn the terms in equation (2).

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$$\int_{T_0}^{\infty} (T-\theta)^n \frac{\partial P}{\partial t} \, dT = \int_{T_0}^{\infty} \left[\frac{\partial}{\partial t}[(T-\theta)^n P] - P\frac{\partial}{\partial t}(T-\theta)^n \right] dT$$

$$= \frac{d}{dt} \int_{T_0}^{\infty} (T-\theta)^n P \, dT + n\frac{d\theta}{dt} \int_{T_0}^{\infty} (T-\theta)^{n-1} P \, dT$$

$$= \frac{dM_n}{dt} + nM_{n-1}\frac{d\theta}{dt}$$

$$K \int_{T_0}^{\infty} (T-\theta)^n P \, dT = KM_n$$

$$K \int_{T_0}^{\infty} (T-\theta)^n (T-T_0)\frac{\partial P}{\partial T} \, dT = K \int_{T_0}^{\infty} (T-\theta)^n (T-\theta+\theta-T_0)\frac{\partial P}{\partial T} dT$$

$$= K \int_{T_0}^{\infty} (T-\theta)^{n+1}\frac{\partial P}{\partial T} dT + K(\theta-T_0) \int_{T_0}^{\infty} (T-\theta)^n \frac{\partial P}{\partial T} dT$$

$$= K \int_{T_0}^{\infty} \left[\frac{\partial}{\partial T}[(T-\theta)^{n+1} P] - P(n+1)(T-\theta)^n \right] dT$$

$$+ K(\theta-T_0) \int_{T_0}^{\infty} \left[\frac{\partial}{\partial T}[(T-\theta)^n P] - nP(T-\theta)^{n-1} \right] dT$$

$$= -(n+1)KM_n - nK(\theta-T_0)M_{n-1}$$

$$-K(T_0-\theta)^{n+1}P(T_0) - K(\theta-T_0)(T_0-\theta)^n P(T_0)$$

where we have used the condition that $\lim\limits_{T \to \infty} P(T,t) = 0$.

Thus we find

$$K \int_{T_0}^{\infty} (T-\theta)^n (T-T_0)\frac{\partial P}{\partial T} dT = -(n+1)KM_n - nK(\theta-T_0)M_{n-1}$$

Nothing can be done with the term

$$\int_{T_0}^{\infty} (T-\theta)^n p(T)P(T) \, dT$$

The term $\displaystyle\int_{T_0}^{\infty} (T-\theta)^n p(T-q) P(T-q)\, dT$ can be rewritten by letting $T = y+q$. It becomes

$$\int_{T_0-q}^{\infty} (y-\theta+q)^n p(y) P(y)\, dy$$

If we remember that $P(y) = 0$ for $y < T_0$ we can change the lower limit to T_0 and if we now replace y by T we get

$$\int_{T_0}^{\infty} (T-\theta+q)^n p(T) P(T)\, dT$$

Putting all these terms together we get the moment equation,

$$\frac{dM_n}{dt} + n M_{n-1}\frac{d\theta}{dt} = - nKM_n - nK(\theta-T_0)M_{n-1}$$
$$+ \int_{T_0}^{\infty} p(T) P(T)[(T+q-\theta)^n - (T-\theta)^n]\, dT$$

The first few equations are:

n=0
$$\frac{dM_0}{dt} = 0$$
Remember that $M_0 = 1$ by definition.

n=1
$$\frac{dM_1}{dt} + M_0\frac{d\theta}{dt} = -KM_1 + K(\theta-T_0)M_0 + \int_{T_0}^{\infty} p(T) P(T) q\, dT$$

But if we remember that $M_0 = 1$ and $M_1 = 0$ by definition, this becomes

$$\frac{d\theta}{dt} = - K(\theta-T_0) + q \int_{T_0}^{\infty} p(T) P(T)\, dT$$

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$\underline{n=2}$ $\quad \dfrac{d\Delta}{dt} + 2K\Delta \approx \displaystyle\int p(T)P(T)[q^2 + 2q(T-\theta)]\,dT$

$\underline{n=3}$ $\quad \dfrac{dM_3}{dt} + 3KM_3 + 3\Delta\dfrac{d\theta}{dt} = -3K(\theta - T_0)\Delta$

$\qquad\qquad + \displaystyle\int p(T)P(T)[q^3 + 3q^2(T-\theta) + 3q(T-\theta)^2]\,dT$

The higher order equations may be simplified by using the θ equation to eliminate $\dfrac{d\theta}{dt}$. If we do this we find for $n \geqslant 2$

$$\dfrac{dM_n}{dt} + nKM_n = -nqM_{n-1}\int pP\,dT = \int pP[(T-\theta+q)^n - (T-\theta)^n]\,dT$$

We then have the following set of equations for the moments:

$$
\begin{aligned}
&M_0 = 1 \\[4pt]
&M_1 = 0 \\[4pt]
&\dfrac{d\theta}{dt} + K\theta = KT_0 + q\int pP\,dT \\[4pt]
&\dfrac{d\Delta}{dt} + 2K\Delta = \int pP[q^2 + 2q(T-\theta)]\,dT \\[4pt]
&\dfrac{dM_3}{dt} + 3KM_3 = \int pP[q^3 + 3q^2(T-\theta) + 3q(t-\theta)^2 - 3q\Delta]\,dT \\[4pt]
&\text{etc.}
\end{aligned}
\qquad (6)
$$

We must now show how $P(T,t)$ can be obtained from the moments. To do this we develop P in a series of

Hermite functions.

$$P(T,t) = \frac{1}{\sqrt{2\pi a}} \, e^{-s^2} \sum_{n=0}^{\infty} C_n(t) H_n(s) \tag{7}$$

where $s = \dfrac{T-\theta}{\sqrt{2a}}$

H_n = the Hermite polynomial of order n.

a is an arbitrary parameter which will be fixed

in a moment.

Such a development is always possible. Using this

development, we may calculate the moments of P. This

is an easy matter if use is made of the orthogonality

properties of the Hermite polynomials. The results are:

$M_0 = C_0$ hence $C_0 = 1$

$M_1 = C_1$ hence $C_1 = 0$ since $M_1 = 0$

$M_2 \equiv \Delta = a + 4aC_2$ thus if we put $a = \Delta$ then $C_2 = 0$.

$M_3 = 6(2a)^{3/2} C_3 = 6(2\Delta)^{3/2} C_3$

or $C_3 = \dfrac{1}{6(2\Delta)^{3/2}} M_3$

In general

$$C_n = \frac{1}{\sqrt{\pi}} \sum_m \frac{(-1)^m}{m!(n-2m)!} \frac{N_{n-2m}}{2^{am}}$$

with $N_n = \dfrac{\sqrt{\pi}}{(2\Delta)^{n/2}} M_n$

We see that a knowledge of the M's determines the C's and

thus $P(T,t)$. We have

$$P(T,t) = \frac{1}{\sqrt{2\pi\Delta}} \, e^{-s^2} \left[1 + \frac{1}{6(2\Delta)^{3/2}} M_3 H_3(s) + \ldots \right] \tag{8}$$

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where $s = \dfrac{T-\theta}{\sqrt{2\Delta}}$. It is clear that choosing $a = \Delta$ gives the simplest possible expression for P in terms of the moments.

<u>Section III</u>. The Saddle Point Method.

We now show how the moment equations (6) may be solved. The difficulty lies in handling the terms involving $p(T)$ on the right-hand side of the equations. We note from equation (8) that if M_3 is small enough to be neglected, then P assumes a very simple Gaussian form $P(T,t) = \dfrac{1}{\sqrt{2\pi\Delta}}\, e^{-s^2}$. Thus in the θ equation we need to treat the following integral

$$I = \frac{qU}{\sqrt{2\pi\Delta}} \int_{T_0}^{\infty} e^{-1/T}\, e^{-\frac{(T-\theta)^2}{2\Delta}} \, dT$$

In the Δ equation we have the integral

$$J = \frac{U}{\sqrt{2\pi\Delta}} \int_{T_0}^{\infty} e^{-1/T}\, e^{-\frac{(T-\theta)^2}{2\Delta}} \, [q^2 + 2q(T-\theta)]dT$$

Since we are neglecting M_3, we go no further than the Δ equation.

If Δ is small, the integrands of both I and J are very strongly peaked at $T = \theta$ because of the factor $e^{-\frac{(T-\theta)^2}{2\Delta}}$. It would therefore be a good approximation to treat the rest of the integrand as a constant equal to its value at $T = \theta$. In this approximation I becomes

$$I = \frac{qU}{\sqrt{2\pi\Delta}}\, e^{-1/\theta} \int_{T_0}^{\infty} e^{-\frac{(T-\theta)^2}{2\Delta}} \, dT$$

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We commit negligible error by replacing the lower limit T_0 by $-\infty$ and the integral is then trivial. We get

$$I = qUe^{-1/\theta}$$

In the same fashion

$$J = q^2Ue^{-1/\theta}$$

These results can be improved upon by the saddle point method. Use of the saddle point method allows Δ to be larger. Let us apply the saddle point method to I. We write

$$I = \frac{qU}{\sqrt{2\pi\Delta}} \int_{T_0}^{\infty} e^{1/\Delta \, F(T)} \, dT$$

where

$$F(T) = -\Delta/T - \tfrac{1}{2}(T-\theta)^2$$

If we plot $F(T)$, we have roughly the following:

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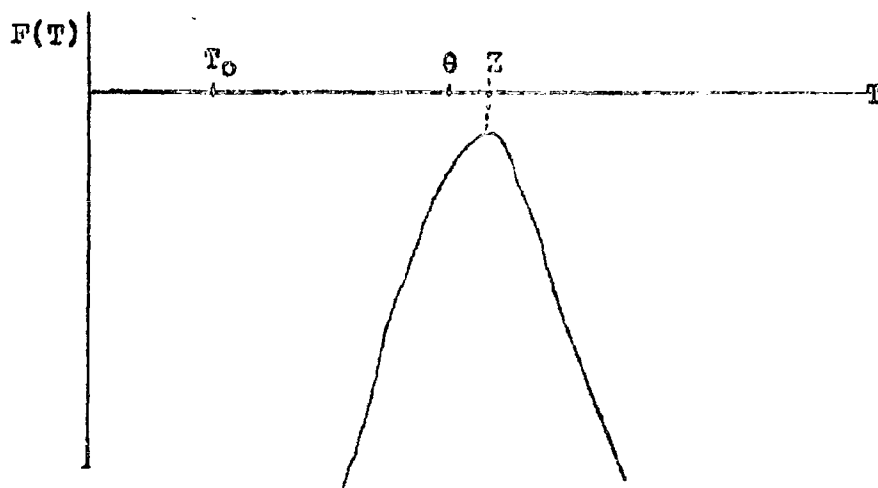
We see that F is peaked near $T = 0$ and falls off very rapidly to large negative values on either side. Thus the major contribution to the integral comes from the neighborhood of the peak and the smaller Δ is the more nearly is this true. The peak of F is at $T = Z$ and Z may be found by putting $F'(T) = 0$. Hence

$$F'(T) = \Delta/T^2 \qquad (T-\theta)$$

and Z is defined implicitly by

$$\Delta/Z^2 - (Z-\theta) = 0$$

or

$$Z = \theta + \Delta/Z^2$$

We see that the smaller Δ is, the nearer is Z to θ. The saddle point method now consists of expanding F(T) about $T = Z$.

$$F(T) = F(Z) + F'(Z)(T-Z) + \tfrac{1}{2}F''(Z)(T-Z)^2 + \ldots$$

If we define $R = \Delta/Z^3$

$$G^2 = 1 + 2R$$

it is readily seen that

$$F(Z) = -\Delta/Z(1+\tfrac{1}{2}R)$$
$$F'(Z) = 0$$
$$F''(Z) = -G^2$$
$$F'''(Z) = 6R/Z$$
$$F^{(n)}(Z) = -(-1)^n \frac{n!R}{Z^{n-2}}$$

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We now write I as

$$I = \frac{qU}{\sqrt{2\pi\Delta}} \int_{T_0}^{\infty} e^{1/\Delta[F(Z)+\frac{1}{2}F''(Z)(T-Z)^2+\ldots]} dT$$

$$= \frac{qU}{\sqrt{2\pi\Delta}} e^{F(Z)/\Delta} \int_{-T_0}^{\infty} e^{-G^2(T-Z)^2/2\Delta} dT$$

where we have neglected higher terms in the expansion of F(T). If again we replace the lower limit by $-\infty$ we have a simple Gauss integral and we obtain

$$I = qU \frac{e^{F(Z)/\Delta}}{G} = \frac{qU}{G} e^{-(1+\frac{1}{2}R)/Z}$$

We note that for very small Δ; $R \approx 0$, $G \approx 1$ and $Z \approx \theta$ which gives us $I = qUe^{-1/\theta}$ as before.

The J integral is treated in similar fashion. We write

$$J = \frac{U}{\sqrt{2\pi\Delta}} \int_{T_0}^{\infty} e^{F(T)/\Delta} [q^2+2q(T-Z+Z-\theta)] dT$$

$$= \frac{U}{\sqrt{2\pi\Delta}} [q^2+2q(Z-\theta)] \int_{T_0}^{\infty} e^{F(T)/\Delta} dT$$

$$+ \frac{2qU}{\sqrt{2\pi\Delta}} \int_{T_0}^{\infty} (T-Z) e^{F(T)/\Delta} dT$$

The first integral is the one we have already treated and the second integral vanishes in the approximations we have made. Therefore

$$J = \frac{qU}{G} [q+2(Z-\theta)] e^{F(Z)/\Delta}$$

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It is not necessary to neglect the higher powers of $(T-Z)$ in the expansion of $F(T)$. We present below the results to the next order of accuracy. The details are rather involved and we refer the reader to Morse and Feshbach "Methods of Mathematical Physics" for a general treatment of the saddle point method.

In summary:

$$I = \frac{qU}{G}e^{F(Z)/\Delta}[1-B_1+B_2]$$

$$J = \frac{qU}{G}e^{F(Z)/\Delta}[(q+2RZ)(1-B_1+B_2)-2(B_{11}+B_{12})]$$

where $Z = \theta + \Delta/Z^2$ $\qquad$ $F(Z) = -\Delta(1+\tfrac{1}{2}R)/Z$

$\qquad R = \Delta/Z^3$

$\qquad G^2 = 1+2R$

$\qquad B_1 = \frac{R^2 Z}{G^6}(3-3R/2)$ $\qquad\qquad$ (9)

$\qquad B_2 = -\frac{R^3 Z^2}{G^{12}}(15-67.5R+22.5R^2-15R^3/8)$

$\qquad B_{11} = 3\frac{R^2 Z^2}{G^4}$

$\qquad B_{12} = 15/2\frac{R^3 Z^3}{G^{10}}(2-6R+R^2)$

The B terms are those which arise from the higher order saddle point treatment of the integrals. These terms are negligible if Δ is sufficiently small.

It should be mentioned that these same techniques are still applicable if the higher moments $(M_3, \text{etc.})$

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are not neglected. It is then necessary to use the saddle point method to a higher order of accuracy.

We are thus faced with the problem of solving equations (6) and (9). With the neglect of M_3 these become

$$\frac{d\theta}{dt} + K\theta = KT_0 + I$$

$$\frac{d\Delta}{dt} + 2K\Delta = J$$

(10)

with I and J defined by (9). The initial conditions are

$$\theta(0) = T_0 + q$$

$$\Delta(0) = 0$$

(11)

The equations (9), (10) and (11) form a closed system which can be integrated numerically. This system was programmed for the IBM 650 computer and twenty hours of computation were carried out. These computations soon indicated that although $\Delta = 0$ for $t = 0$, it rather quickly grows to such a large value as to invalidate the approximations made earlier on the assumption that Δ was small. Further, as Δ grows in size this is an indication that the higher moments, M_3 etc., are also becoming important. We see, therefore, that the above techniques, which in principle will yield a solution, are in practice much too tedious to be useful. In the next section we see how this difficulty can be circumvented. The techniques we have developed in Sections II and III are still applicable but in slightly altered form.

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Section IV. Improved Solution

The equation we wish to solve is

$$\frac{\partial P}{\partial t} - KP = K(T-T_0)\frac{\partial P}{\partial T} - p(T)P(T) + p(T-q)P(T-q) \qquad (2)$$

with the initial condition: $P(T,0) = \delta(T-T_0-q)$.

Now if there were no reactions occurring, the initial δ function distribution would move to lower temperature with time but would remain a δ function. In fact, if we define $Y(t)$ to be the solution of the equation:

$$\frac{dY}{dt} = -K(Y-T_0) \quad Y(0) = T_0 + q \qquad (12)$$

it is clear that $Y(t)$ represents the temperature our "point" would have if it simply loses heat by conduction — no reactions.

It is now evident that $P(T,t) = \delta(T-Y(t))$ should satisfy (2) with the reaction terms omitted; namely

$$\frac{\partial P}{\partial t} - KP = K(T-T_0)\frac{\partial P}{\partial T} \qquad (13)$$

To verify this note:

$$\frac{\partial P}{\partial t} = -\frac{dY}{dt}\delta'(T-Y), \quad \frac{\partial P}{\partial T} = \delta'(T-Y)$$

Substituting in (13) we find

$$-\frac{dY}{dt}\delta'(T-Y) - K\delta(T-Y) = K(T-T_0)\delta'(T-Y)$$

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or $\left[K(T-T_0) + \frac{dY}{dt}\right] \delta'(T-Y) + K \delta(T-Y) \stackrel{?}{=} 0$

Now using (12)

$$\left[K(T-T_0) - K(Y-T_0)\right] \delta'(T-Y) + K \delta(T-Y) \stackrel{?}{=} 0$$

$$K(T-Y) \delta'(T-Y) + K \delta(T-Y) \stackrel{?}{=} 0$$

Using the property of the δ function that
$x \delta'(x) = -\delta(x)$ we have

$$- K \delta(T-Y) + K \delta(T-Y) = 0 \qquad \text{qed.}$$

Let us now consider the effect of reactions. The
δ function will not only sink to lower temperature
because of heat conduction, it will also decrease in
amplitude due to the occurrence of reactions. This we
may take care of by writing

$$A(t) \delta(T-Y(t)) \quad \text{with } A(0) = 1.$$

As time elapses the probability of a reaction increases
and this means the function $P(T)$ will begin to grow a
little bump in the neighborhood of the temperature T_0+2q.
The probability at T_0+2q will also be undergoing reactions
thereby building up a probability bump in the neighborhood
of T_0+3q. Thus after a short time we would expect $P(T)$
to have the indicated character.
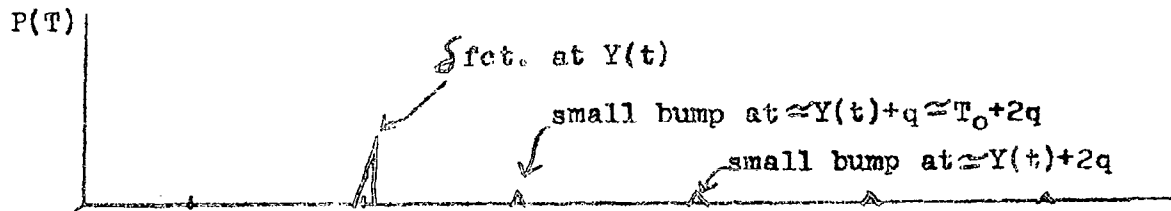
This picture suggests trying a solution of the form:

$$P(T,t) = A(t) \, \delta(T-Y(t)) + \sum_{m=1}^{\infty} A_m(t) \, u_m(T,t) \qquad (14)$$

The u_m's will be taken as normalized so that $\int u_m \, dT = 1$. Also u_m is localized in the neighborhood $T \simeq Y + nq$. Thus the problem becomes one of determining the A's as functions of time and the u_m's as functions of T and t.

We now substitute (14) into (2). Because P(T) is different from zero only in well separated regions, we may consider individually the various regions. Consider first the region in the vicinity of $T = Y(t)$. What terms in Eq. (2) contribute in this region? It is easy to see that we have:

$$[\mathring{A}-KA + p(T)A]\, \delta(T-Y) - [\mathring{Y} + K(T-T_0)] \, A\delta'(T-Y)$$

and these terms should equal zero.
Now using (12) we have

$$\mathring{Y} + K(T-T_0) = -K(Y-T_0) + K(T-T_0) = K(T-Y)$$

Remembering that $x \delta'(x) = -\delta(x)$ we get

$$[\mathring{A} - KA + p(T)A] \delta'(T-Y) - KA(T-Y) \underbrace{\delta''(T-Y)}_{-\delta'(T-Y)} = 0$$

Hence $[\mathring{A} - KA + p(T)A + KA] \delta'(T-Y) = 0$

or

$$(\mathring{A} + p(T)A) \delta'(T-Y) = 0$$

Because of the δ function we may also write this as

$$(\mathring{A} + p(Y)A) \delta'(T-Y) = 0$$

For this to vanish we find

$$\boxed{\mathring{A} = -p(Y)A} \qquad (15)$$

This result could clearly have been written down immediately. It simply says that the amplitude of the δ function at $Y(t)$ changes due to the reactions which occur.

Consider now the terms which contribute in the neighborhood of $Y(t) + q$. These terms are:

$$\mathring{A}_1 u_1 + A_1 \mathring{u}_1 - KA_1 u_1 = K(T-T_0)A_1 \frac{\partial u_1}{\partial T} - p(T)A_1 u_1 \qquad (16)$$

$$+ p(T-q) \ A\delta(T-q-Y)$$

Note that the term $p(T-q) \ P(T-q)$ in (2) furnishes the connection between the two regions.

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For $m \geq 2$ we have in general

$$\mathring{A}_m u_m + A_m \mathring{u}_m - K A_m u_m = K(T - T_0) A_m \frac{\partial u_m}{\partial T} - p(T) A_m u_m$$

$$+ p(T-q) A_{m-1} u_{m-1}(T-q) \tag{17}$$

How shall we solve these equations? Eq. (15) is of course no trouble, but how do we treat (16) and (17)? The moment technique is applicable.

Let us define:
$$\theta_m = \int T u_m dT$$

and
$$M_{nm} = \int T \theta_m^{\ n} u_m dT$$

Consider now Eq. (16). We will suppress the $m = 1$ subscript and write M_n, θ, u rather than M_{1n}, θ_1, u_1. Multiply (16) by $(T-\theta)^n$ and integrating we meet the following terms

$$A_1 \int (T-\theta)^n \mathring{u} dT = \mathring{A}_1 M_n$$

$$A_1 \int (T-\theta)^n \mathring{u} dT = A_1 \left[\frac{d}{dt} \int (T-\theta)^n u dT + \int (T-\theta)^{n-1} m \mathring{\theta} u dT \right]$$

$$= A_1 \left[\mathring{M}_n + n \mathring{\theta} M_{n-1} \right]$$

$$- K A_1 \int (T-\theta)^n u dT = - K A_1 M_n$$

$$K A_1 \int (T-T_0)(T-\theta)^n \frac{\partial u_1}{\partial T} dT = K A_1 \int (T-\theta+\theta-T_0)(T-\theta)^n \frac{\partial u_1}{\partial T} dT$$

$$= K A_1 \left[\int (T-\theta)^{n+1} \frac{\partial u}{\partial T} dT + (\theta-T_0) \int (T-\theta)^n \frac{\partial u}{\partial T} dT \right]$$

$$= K A_1 \left[-(n+1) \int (T-\theta)^n u dT - n(\theta-T_0) \int (T-\theta)^{n-1} u dT \right]$$

$$= - K A_1 \left[(n+1) M_n + n(\theta-T_0) M_{n-1} \right]$$

$$- A_1 \int (T-\theta)^3 \, p(T) u(T) dT \quad \text{which cannot be simplified}$$

$$+ A \int (T-\epsilon)^n \, p(T-q) \int (T-q-Y) dT = A(q+Y-\theta)^n \, p(Y)$$

Putting these all together we find:

$$\dot{A_1} M_n + A_1 \left\{ \ddot{M}_n + nk M_n + n M_{n-1} \dot{\theta} \right\} = - nk(\theta - T_0) A_1 M_{n-1} \tag{18}$$

$$- A_1 \int (T-\theta)^n \, p(T) u(T) dT + A p(Y)(Y+q-\theta)^n$$

By definition $M_0 = 1$, $M_1 = 0$. Consider (18) for various n.

<u>$n = 0$</u> $A_1 \quad A p(Y) = A_1 \int p(T) u(T) dT$

<u>$n = 1$</u> $A_1 \dot{\theta} = - K(\theta - T_0) A_1 + A p(Y)(Y+q-\theta) - A_1 \int (T-\theta) p(T) u(T) dT$

<u>$n = 2$</u>   Denote M_2 by Δ

$$\dot{A_1} \Delta + A_1 \left\{ \ddot{\Delta} + 2K\Delta \right\} = + A p(Y)(Y+q-\theta)^2$$

$$- A_1 \int (T-\theta)^2 p(T) u(T) dT$$

We may use the $n = 0$ equation to eliminate $\dot{A}$ from the $n=2$ equation.

$$A_1 \left\{ \dot{\Delta} + 2K\Delta \right\} = A p(Y) \left\{ (Y+q-\theta)^2 - \Delta \right\}$$

$$- A_1 \int \left\{ (T-\theta)^2 - \Delta \right\} p(T) u(T) dT$$

If we assume the higher moments are negligible, we are

led to the following system of equations:

$$\dot{A} = -p(Y)A \tag{19a}$$

$$\dot{A}_1 = Ap(Y) - A_1 \int p(T)u(T)dT \tag{19b}$$

$$\dot{\theta} = -K(\theta - T_0) - \int (T-\theta)p(T)u(T)dT + \frac{A}{A_1} p(Y)(Y+q-\theta) \tag{19c}$$

$$\dot{\Delta} = -2K\Delta - \int \left\{ (T-\theta)^2 - \Delta \right\} p(T)u(T)dT + \frac{A}{A_1} p(Y) \left\{ (Y+q-\theta)^2 - \Delta \right\} \tag{19d}$$

Note the interpretation of (19b). A_1 measures the total probability of the first bump (since u is normalized to unit probability). How does A_1 change? It gains from reactions occurring at the δ function [term $Ap(Y)$] and it loses because reactions occur at the first bump causing "transitions" to the second bump [term $-A_1 \int p(T)u(T)dT$]. u is of course still an unknown function. However, it can be expanded in Hermite functions just as P was in Section II.

$$u(T,t) = \frac{1}{\sqrt{2\pi\Delta}} e^{-\frac{(T-\theta)^2}{2\Delta}} \sum C_n(t) H_n\left(\frac{T-\theta}{\sqrt{2\Delta}}\right) \tag{20}$$

The coefficients C_n are related to the moments. It is easy to show that

$$C_0 = M_0 = 1$$

$$C_1 = M_1 = 0$$

$$C_2 = \frac{M_2 - \Delta}{4\Delta} = 0 \qquad \text{since } M_2 = \Delta$$

Note: C_1 and C_2 vanish because we defined θ as the mean of u and Δ as the mean square derivation of u.

$$C_3 = \frac{1}{6(2\Delta)^{3/2}} M_3$$

$$C_3 = \frac{1}{\sqrt{\pi}} \sum_K \frac{(-1)^K}{K!(5-2K)!} \frac{N_{3-2K}}{2^{2K}} \qquad N_r = \frac{\sqrt{\pi}}{(2\Delta)^{r/2}} M_r$$

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Since we assume M_3 and higher are negligible we get

$$u = \frac{1}{\sqrt{2\pi\Delta}} \; e^{-\frac{(T-\theta)^2}{2\Delta}} \tag{21}$$

The u in (19) is to be interpreted as (21) and then equations (19) form a closed system for the quantities A, A_1, θ, Δ, all of which are functions of t.

The saddle point method of Section III may be applied without change to the integrals of (19). Omitting the B terms we have

$$\int p(T)u(T)\,dT = \frac{U}{G} \; e^{-(1+\frac{1}{2}R)/Z}$$

$$\int (T-\theta)p(T)u(T)\,dT = (Z-\theta)\frac{U}{G} \; e^{-(1+\frac{1}{2}R)/Z}$$
$$= \frac{\Delta U}{Z^2 G} \; e^{-(1+\frac{1}{2}R)/Z} \tag{22}$$

$$\int [(T-\theta)^2 - \Delta]p(T)u(T)\,dT = [Z-\theta)^2 - \Delta + \frac{\Delta}{2G^2}]$$
$$\frac{U}{G} \; e^{-(1+\frac{1}{2}R)/Z}$$

It must be remembered that we have been looking at the first bump and that many quantities in equations (19) and (22) need the subscript "1".

The higher bumps, $m \geqslant 2$, are treated in exactly the same fashion. The only difference is that the δ function is no longer present for $m \geqslant 2$ and therefore those terms

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in (19b), (19c), and (19d) which involve Y are replaced by integrals.

We give below the complete set of equations for the $\mathscr{J}$ function and the first two bumps. The equations for all higher bumps are obtained from those for $m = 2$ by simply changing subscripts.

$$
\begin{aligned}
\underline{m=0} \quad & \mathring{A} = -p(Y)A \\
& \mathring{A}_1 = Ap(Y) - A_1 \int_{T_0}^{\infty} p(T)u_1(T)\,dT \\
& \mathring{\theta}_1 = -k(\theta_1 - T_0) - \int_{T_0}^{\infty}(T-\theta_1)p(T)u_1(T)\,dT \\
& \qquad\qquad + \frac{A}{A_1}p(Y)(Y+q-\theta_1) \\
\underline{m=1} \quad & \mathring{\Delta}_1 = -2k\Delta_1 - \int_{T_0}^{\infty}[(T-\theta_1)^2 - \Delta_1]p(T)u_1(T)\,dT \\
& \qquad\qquad + \frac{A}{A_1}p(Y)[(Y+q-\theta_1)^2 - \Delta_1] \qquad\qquad (23)
\end{aligned}
$$

The integrals are given by (22) with $\theta = \theta_1$, $Z = Z_1$, $\Delta = \Delta_1$, $G = G_1$, $R = R_1$. Z, G, and R have the same definitions as given in Section III.

$$
\begin{aligned}
\underline{m=2} \quad & \mathring{A}_2 = A_1 \int_{T_0}^{\infty} p(T)u_1(T)\,dT - A_2 \int_{T_0}^{\infty} p(T)u_2(T)\,dT \\
& \mathring{\theta}_2 = -k(\theta_2 - T_0) - \int_{T_0}^{\infty}(T-\theta_2)p(T)u_2(T)\,dT \\
& \qquad\qquad + \frac{A_1}{A_2}\int_{T_0}^{\infty}(T+q-\theta_2)p(T)u_1(T)\,dT \\
& \mathring{\Delta}_2 = -2k\Delta_2 - \int_{T_0}^{\infty}[(T-\theta_2)^2 - \Delta_2]p(T)u_2(T)\,dT \\
& \qquad\qquad + \frac{A_1}{A_2}\int_{T_0}^{\infty}[(T+q-\theta_2)^2 - \Delta_2]p(T)u_1(T)\,dT
\end{aligned}
$$

The integrals involving u_2 are given by (22) with $\theta = \theta_2$, $Z = Z_2$, $\Delta = \Delta_2$, etc. The integrals

involving U_1 are slightly different.

$$\int_{T_0}^{\infty} (T+q-\theta_2)p(T)u_1(T)\,dT = (Z_1+q-\theta_2)\frac{U}{G_1}\,e^{-(1+\frac{1}{2}R_1)/Z_1}$$

$$\int_{T_0}^{\infty} [(T+q-\theta_2)^2-\Delta_2]p(T)u_1(T)\,dT = [\frac{\Delta_1}{2G_1^2} + (Z_1+q-\theta_2)^2-\Delta_2]$$

$$\times \frac{U}{G_1}\,e^{-(1+\frac{1}{2}R_1)/Z_1}$$

The initial conditions are

$$A = 1, \quad A_m = 0 \text{ for } m \geq 1$$

$$\theta_m = T_0 + (m+1)q$$

$$\Delta_m = 0$$

This system is amenable to solution on a computer. It has, in fact, been programmed and preliminary calculations carried out. The results indicate that the bumps remain very narrow and therefore that the approximations based on small Δ are very good.

The actual calculations are, however, performed with the modifications of the next section.

Section V. The Expanding Single Point Model.

As indicated in the introduction, it is possible with minor modifications to convert the "single-point" model into a much more realistic model. It is the purpose of this section to indicate these changes. They are two in number; one serves to remove the restriction to a fixed

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number of molecules in the heated region - thus we term this the "expanding single point" model. The other change takes into account the fact that when a molecule reacts it is then unavailable for further reactions.

If an amount of energy Q is released at a point in a medium at $t = 0$, then the heat conduction equation predicts a spherical temperature distribution given by

$$T(r,t) = \frac{Q}{8\pi^{3/2}C} \frac{1}{(Dt)^{3/2}} e^{-\frac{r^2}{4Dt}} + T_0 \qquad (24)$$

where C is the heat capacity per unit volume.

$$D = \frac{k}{C} \qquad k \text{ is the thermal conductivity.}$$

T_0 is the initial temperature of the medium. This temperature distribution is quite well approximated by a distribution which is constant from $r = 0$ to $r = \sqrt{4Dt}$ and drops to T_0 for $r > \sqrt{4Dt}$. In order to conserve heat energy the constant value of T must be

$T = T_0 + \frac{Q}{8C(\frac{4\pi}{3})} \frac{1}{(Dt)^{3/2}}$. Thus we approximate (24) by

$$T(r,t) = T_0 + \frac{3}{32\pi} \frac{Q}{C} \frac{1}{(Dt)^{3/2}} \qquad r < \sqrt{4Dt}$$

$$\qquad\qquad\qquad (25)$$

$$= T_0 \qquad\qquad\qquad r > \sqrt{4Dt}$$

The heated region is now seen to be expanding with a radius proportional to $\sqrt{t}$. The volume of and therefore the number of molecules in the heated region grows proportional to $t^{3/2}$.

The quantity K introduced in Section I described the change in temperature of the "point" due to heat conduction and was so chosen that

$$\frac{dT}{dt} = -K(T-T_0)$$

If we differentiate (25) we find

$$\frac{dT}{dt} = \frac{3}{32\pi} \frac{Q}{C} \left(\frac{-3/2 D}{(Dt)^{5/2}}\right) = -\frac{3}{2} \frac{1}{t} \left[\frac{3}{32\pi} \frac{Q}{C} \frac{1}{(Dt)^{3/2}}\right]$$

$$= -\frac{3}{2} \frac{1}{t} (T-T_0)$$

Thus we may identify the K of the preceding four sections with $-\frac{3}{2} \frac{1}{t}$, in order to go to the expanding point model. The fact that K is now a function of time in no way invalidates our previous development.

If now a second reaction occurs we again have an energy release of amount Q. We must now assume that this energy is distributed uniformly over a region of radius $\sqrt{4Dt}$ in order once again to preserve the single point character of the model. It is easily seen, from energy considerations, that this will produce a rise in

temperature in the amount

$$q = \frac{3}{32\pi} \frac{Q}{C} \frac{1}{(Dt)^{3/2}}$$

Therefore the q of the preceding sections is now to be taken as a function of t rather than a constant. Again, all previous work is valid with this change.

Now what changes are necessary to take into account the loss of available molecules as reactions occur. We can introduce a characteristic radius, r_o, such that $\frac{4}{3}\pi r_o^3 = v_o$, the volume per molecule. This leads to a characteristic time t_o which is equal to the time it takes the heat pulse (25) to spread out over the region occupied by a single molecule. It is now clear that no reactions can occur until $t \gg t_o$ because only then has the heat pulse begun to move into a region where unused molecules are available. We see then that the number of molecules available for reaction at any time is proportional to $(t^{3/2} - t_o^{3/2})$. We should therefore write $p(T)$ as $Ue^{-1/T}$ where $U = V(t^{3/2} - t_o^{3/2})$ with $V = \frac{A}{t_o^{3/2}}$. A is the frequency factor of the Arrhenius equation.

These remarks are valid if only one reaction has occurred. If, however, two reactions have taken place, we have used up two molecules and we should put $U = V(t^{3/2} - 2t_o^{3/2})$. Hence, in the language of Section IV, we see that when we calculate with $p(T)$ at the δ function peak, we should set U equal to $V(t^{3/2} - t_o^{3/2})$. When we calculate with $p(T)$ at the first bump, we must set U equal to $V(t^{3/2} - 2t_o^{3/2})$.

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At the second bump $U = V(t^{1/2} - 3t_o^{3/2})$, etc. In all these expressions if t is such as to make U negative, then U is actually zero.

We see that the higher bumps are only activated after an appropriate interval of time. Thus the first bump only begins to appear when $t > t_o$, the second bump when $t > 2^{2/3}t_o$, etc. This has the effect of changing the initial conditions associated with equations (23). It is clear that the calculations with (23) begin at $t = t_o$. For $t < t_o$, $A = 1$ and $A_m = 0$ for all m. "t_o" is a natural time unit and in the numerical calculations t_o has been set equal to one. The initial conditions for the first bump are:

$$A_1 = 0, \quad \Delta_1 = 0, \quad \theta_1 = Y(t_o) + q(t_o) \text{ when } t = t_o$$

The initial conditions for the second bump are:

$$A_2 = 0, \quad \theta_2 = \theta_1(t_1) + q(t_1), \quad \Delta_2 = \frac{\Delta_1(t_1)}{2\theta_1^2(t_1)}$$

when $t = t_1 = 2^{2/3}t_o$

Similar conditions hold for all higher bumps.

These changes seem to complicate the equations a great deal but, in actual fact, since the computations must be done on a digital computer anyway the complications are relatively minor.

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Section VI. Probability of Initiation.

We come now to the important question of determining the probability that an initial reaction will lead to initiation of explosion. To answer this we must consider the behavior of the bumps with time, in particular the behavior of the bump amplitude, A_m. If we look at some bump, say the mth one, we see that it is gaining probability from the next lower (m-1) bump and losing probability to the next higher (m+1) bump. At the same time all bumps are sinking to lower temperature because of heat conduction. When a bump is first activated it will gain more from below than it loses above. It will thus increase in amplitude for a time. Eventually it will begin to lose more above than it gains from below and the amplitude will start to decrease. Now the m-1 bump eventually sinks to so low a temperature that it no longer feeds the mth bump. The mth bump continues to feed the m+1 bump and now we can envision two possibilities. The first possibility is that the mth bump continues to transfer probability to the m+1 bump so rapidly that its amplitude, A_m, goes to zero before it sinks so low in temperature that it can no longer undergo reactions. The second possibility is just the converse, namely, the mth bump does not empty itself before its temperature gets too low to produce reactions.

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In this case A_m will approach some constant, non-zero value.

In essence, the above paragraph simply states that $\lim_{t \to \infty} A_m$ is either zero or non-zero. However, the above remarks also make clear the fact that if $\lim_{t \to \infty} A_m = 0$ then $\lim_{t \to \infty} A_\ell = 0$ for all $\ell > m$. Also if $\lim_{t \to \infty} A_m$ is non-zero then $\lim_{t \to \infty} A_\ell$ is non-zero for all $\ell < m$. Thus the A's split into two groups defined by some integer $\bar{m}$, such that

$$\lim_{t \to \infty} A_m \neq 0 \qquad m \leq \bar{m}$$

$$\lim_{t \to \infty} A_m = 0 \qquad m > \bar{m}$$

We see that all bumps with $m > \bar{m}$ represent cases where the chain reaction died out and did not lead to an explosion. Therefore the explosion probability is given by

$$1 - \lim_{t \to \infty} (A + A_1 + A_2 + \ldots , A_{\bar{m}}) \qquad (26)$$

The procedure then is to integrate equations (23) out to the last bump for which A does not go to zero. This determines $\bar{m}$ and then (26) gives the probability of explosion.

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Section VII. Numerical Calculations

In order to proceed with numerical calculations, it is necessary to arrive at reasonable estimates for the parameters of the theory. Since at this stage no effort is being made to make a direct comparison with experiment, we are only concerned that the parameters have the proper order of magnitude.

As pointed out previously the quantity T, referred to as temperature, is actually being measured in energy units. That is, T actually signifies the temperature multiplied by Boltzmann's constant. The natural unit for energy is the activation energy E and is of the order of a few electron volts. Since most explosives undergo thermal initiation in the range from 200° to 400°C we have taken T_0, the ambient temperature to be of the order of 600°K. In energy units this is about 1/20 ev. When divided by an activation energy of about 2 ev., this gives a T_0 of about 1/40. Thus we have calculated with a T_0 of the order 0.02.

The quantity q is given in Section V as

$q = \dfrac{3}{32\pi} \dfrac{Q}{C(Dt)^{3/2}}$ which we write as $\dfrac{W}{t^{3/2}}$. Thus

$W = \dfrac{3Q}{32\pi \, CD^{3/2}}$ where

Q is the energy release per reaction

C is the specific heat per unit volume

$D = \dfrac{K}{C}$ where K is the thermal conductivity.

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Specific heats are of the order 0.5 cal/cm^3°C and
thermal conductivities range from 10^{-5} to 10^{-2}
cal cm sec°C. If we take K about 5 x 10^{-4} we find for
D a value of 10^{-3} cm^2/sec. Now the characteristic time
t_o is defined as the time required for the heat pulse
to spread out over the volume occupied by one molecule.
According to equation (25) this means $\sqrt{4Dt_o}$ equals
a molecular radius. The unit cell for the azies has
dimensions of the order 6 A°. Thus if we put D = 10^{-3}
and $\sqrt{4Dt_o}$ = 3 x 10^{-8} we find $t_o \cong$ 2 x 10^{-13} sec. Thus
our time unit will be of the order of 10^{-13} sec.

To find a value for W we proceed as follows. If
we measure time in units of t_o then W is clearly the
temperature rise produced by the reaction after a time
t_o, i.e., after the energy of reaction has spread out
over one molecule. Thus $W = \dfrac{Q}{\frac{32\pi}{3}(Dt_o)^{3/2}C}$. Now
$\frac{32\pi}{3}(Dt_o)^{3/2}$ is just the volume occupied by a single molecule
and is of the order 10^{-22} cm^3. Q, the energy released
per reaction, is of the order 10 ev. and the specific
heat per unit volume is about 1.5 x 10^{19} ev./cm^3°C. These
give for W about 5000°C. Converting to electron volts
we get about .5 ev. We now must divide by the activation
energy E $\sim$ 2 ev. and we finally arrive at W $\sim$ 0.25.

We have written p(T) as $V(t^{3/2}-t_o^{3/2})e^{-1/T}$.
If we measure time in units of t_o this becomes

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$V(t^{3/2}-1)e^{-1/T}$. Now when p(T) is written in the form $p = NAe^{-E/RT}$, as is customary in the chemical literature, A ranges from 10^{13} to 10^{19} sec^{-1}. We must convert to our time unit which will change A to range from 1 to 10^6. N is the number of molecules involved, which in our case should be taken as one. Thus we see that V should range from 1 to 10^6. We have calculated with $V = 10^2$ and 10^3.

The following graphs present the results for calculations with W = .23, V either 10^2 or 10^3 and T_0 either .019 or .02. These calculations were carried out to the third bump with the hope that the value $\overline{m}$ defined in Section VI would be reached. This did not prove to be the case as the results show. The calculations did not extend beyond the third bump because the program, as written, used the full capacity of the IBM 650 computer. However, the results show that the bumps remain much narrower than expected. That is, the quantity Δ_m, which measures the width of the m'th bump, remains very small throughout the calculation. This means that to very good accuracy we may ignore the width of the bumps thereby greatly simplifying the calculations. We have almost completed a new program which can compute an unlimited number of bumps.

Although the calculations presented do not reach the value $\overline{m}$, they do otherwise exhibit exactly the

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$V = 10^3$
$W = 0.23$
$T_o = 0.02$

A, A_1, A_2, A_3

A

A_1

A_2

A_3

1.0   2.0   3.0   4.0

t in units of t_o

1.0

0.8

0.4

0.2

1.0

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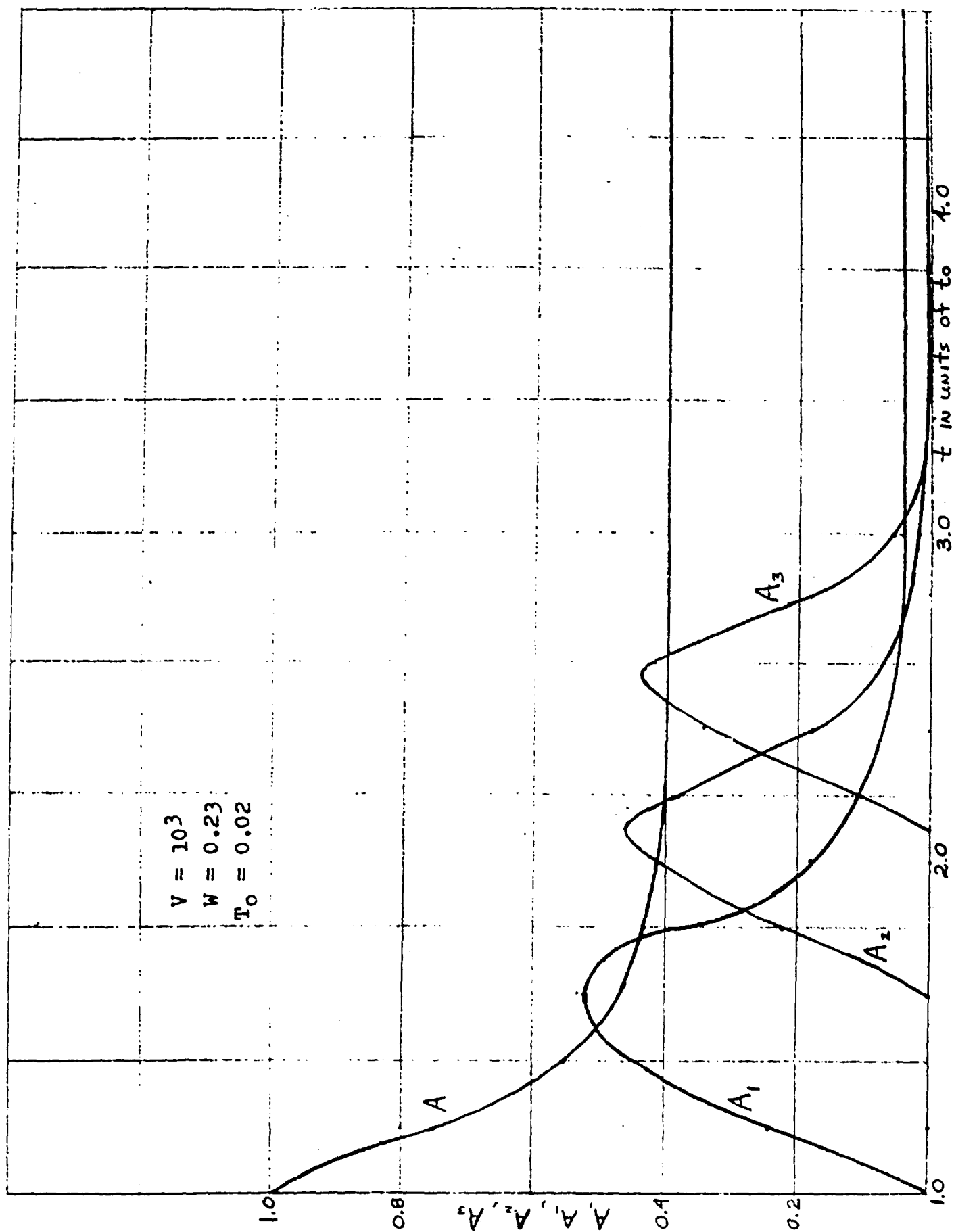
The maximum values reached by the Λ's in this calculation are:

$\Delta_1 = 1.3 \times 10^{-6}$

$\Delta_2 = 2.5 \times 10^{-5}$

$\Lambda_3 = 5 \times 10^{-7}$

$V = 10^8$

$w = 0.23$

$\eta_0 = 0.019$

behavior predicted in Section VI. The bump amplitudes, A_m, start at zero, increase to a maximum and then decrease finally to a constant value.

Section VIII. Conclusions and Recommendations.

The calculations presented are extremely encouraging. We feel that the nearly completed program, designed to calculate an arbitrary number of bumps, will allow us to reach the $\bar{m}$ bumps. This will permit computation of initiation probabilities. We strongly urge the continuation of the computational program.

We have just recently made some progress in an attempt to obtain a completely analytical solution to the "single-point" model. Such a solution would be an extremely valuable addition to the numerical results as it would allow the general nature of the "single-point" model to be more adequately explored. We feel this to be a very promising area of investigation.

Perhaps a few remarks concerning the significance of the model are in order. The model is admittedly much simplified. We feel, however, that it is a significant exploration of the probabilistic aspect of the initiation process. After the changes of Section V, we feel that the only seriously unrealistic aspect of the model which remains is the matter of assuming that the energy Q of a reaction is spread uniformly over the

entire heated region. It is clear that a more realistic treatment of this point would make the probabilistic approach even more necessary.

It is our feeling that a completely adequate treatment of the initiation process might contain the treatment of this report as a bridge between a more detailed treatment of the earliest stages of initiation and the latter stages when the heated region has grown to a macroscopic hot spot for which a probability approach is unnecessary. We have begun to look at possible approaches to the earliest stages of the initiation process and have some indication of progress in this direction.

A MOLECULAR THEORY OF EXPLOSION

M. Mizushima and D. G. Burkhard

<u>Section I.</u> Probability of Reaction as a Function of
Intermolecular Distance.

The potential energy may be plotted as a function of
intermolecular distance as shown schematically in Figure
1. In the diagram r_0
is the equilibrium distance
and the curve I gives the
potential energy as a
function of r. If the temp-
erature is not high,
molecules in a solid will
vibrate about an equilibrium
position in an approximately
simple harmonic way as will
be discussed in the next
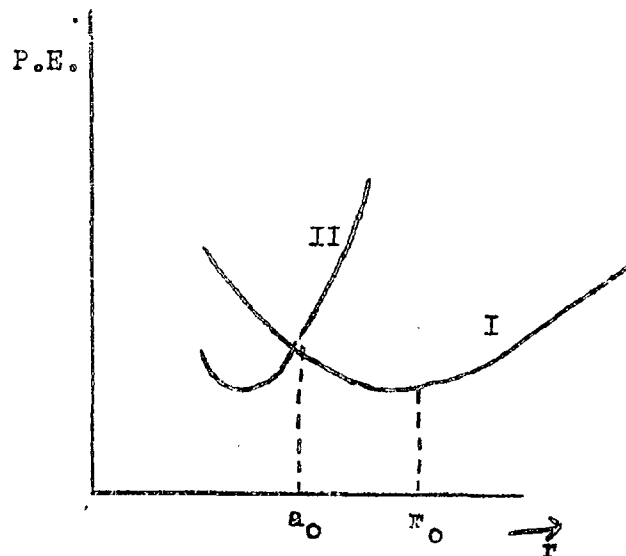
Figure 1

section. If the amplitude of vibration becomes large
enough, the substance can go into new equilibrium config-
uration with potential energy represented by curve II.
If the amplitude becomes larger there will be a probability
of the reaction

$$N_3^{\ldots} + N_3^{\ldots} \longrightarrow 3N_2 + 2e \qquad (1)$$
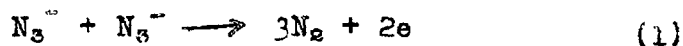
where electrons on the right-hand side are taken up by
the metal ions.

The situation can be illustrated schematically by
means of a series of equipotential energy contours as
shown in Figure 2. In this diagram the potential energy is
expressed as a function of the $N_3^- - N_3^-$ separation and
also as an average of the $N_2 - N_2$ distances. The solid
equipotential curves show potential energy contours when
the $2N_3^-$ configuration is maintained. The dotted equipo-
tential curves schematically represent the potential energy
contours when the nitrogens become predominantly N_2 groups.
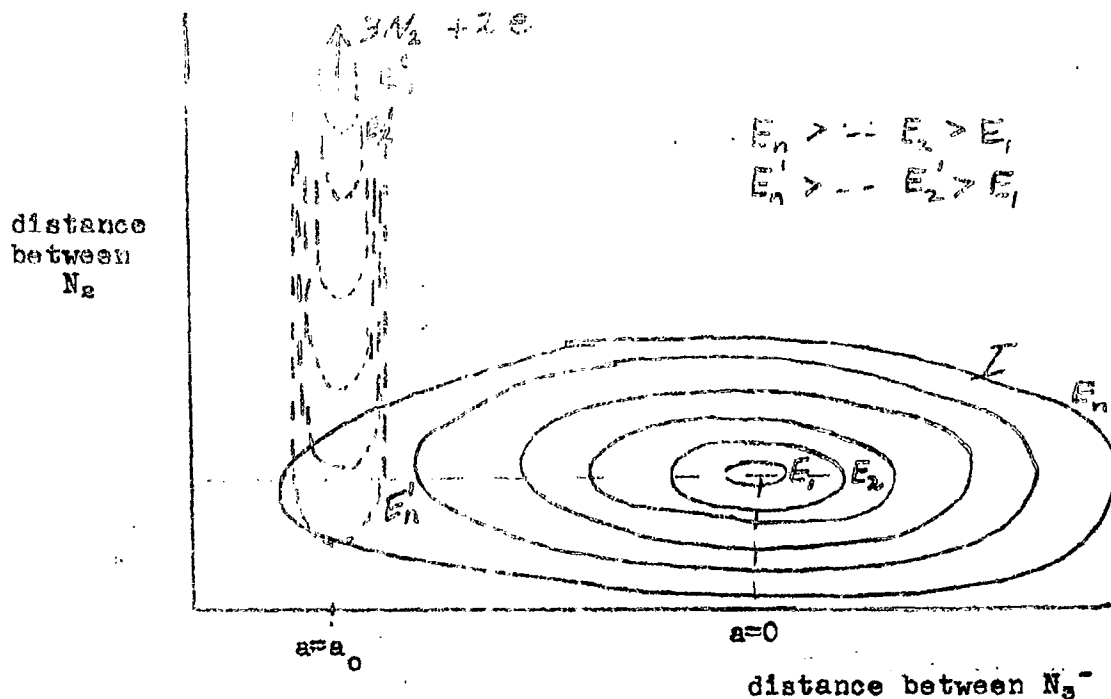
Schematic of Equipotential Contours

Figure 2

Since the configurations have different electronic
structure, the two potential surfaces can co-exist at

each point of this diagram. The minimum of solid-lined potential surface, of course, corresponds to the equilibrium distance of N_3^- ions, while the dotted-line potential surface does not have a minimum except at infinity since N_2 molecules are known to have no bound state (a N_4 molecule). The cross-section of this diagram along the broken straight lines is our Figure 1, where the curve II is for the $3N_2$ configuration.

Reaction (1) can occur if one brings two N_3^- ions along the curve I and crosses the point where $a \approx (r_0 - r)$ is a_0. This a_0 is called the critical amplitude. It is possible, however, that even if the N_3^- ions are put together with distance smaller than this critical amplitude, they come back to the $2N_3^-$ configuration following the curve I. They have to jump into the curve II in order that reaction (1) take place.

The probability that molecules jump from the curve I to the curve II can be assumed to be proportional to the time that the $2N_3^-$ system spends in the region over the critical amplitude a_0. The probability can actually be a rather complicated function of the N_3^- distance. The above assumption corresponds to the simplest case that the probability is constant only if the distance is smaller than this critical amplitude.

The tunnel effect can produce the reaction even if the amplitude of the oscillation is smaller than the critical value, but the probability of a reaction through such a mechanism must be negligible.

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Suppose a_0 is large so that classical mechanics gives a good approximation. If the vibration is simple harmonic, the displacement x is given by

$$x = x_0 \sin \omega t$$

$$\frac{dx}{dt} = \omega \sqrt{x_0^2 - x^2}$$

Fraction of a period spent in time dt is dt/T. Thus the probability that the particle be found in range $x \sim x + dx$ is

$$P dx = \frac{dt}{T} = \frac{dx}{T\omega \sqrt{x_0^2 - x^2}} \quad \frac{dx}{2\pi \sqrt{x_0^2 - x^2}} \tag{2}$$

Let $\mathcal{F} = \mathcal{F}(x)$ be the reaction rate when the particle is at x. If a reaction occurred only for $x = a_0$ then $\int \mathcal{F}(x) \delta(x - a_0) dx = \mathcal{F}(a)$, for example.

If there is a certain probability Pdx of particle being found between x, and x+dx then Pdx gives the number of reactions per unit time while the particle is in the range $x \sim x + dx$. Thus the effective reaction rate for the simple harmonic oscillator is

$$K \equiv \int \mathcal{F}(x) P dx = \frac{1}{\pi} \int_{-x_0}^{x_0} \frac{\mathcal{F}(x) dx}{\sqrt{x_0^2 - x^2}} \tag{3}$$

1. Suppose the reaction rate is such that

$$\mathcal{F}(x) = \mathcal{F}_1 \quad \text{if } x > a_0$$
$$= 0 \quad \text{if } x < a_0 \tag{4}$$

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where ξ_1 is a constant. The effective reaction rate K is, from equation (3)

$$K_1 = \xi_1 \int_{a_0}^{x_0} \frac{dx}{\pi \sqrt{x_0^2 - x^2}} = \xi_1 f \tag{5}$$
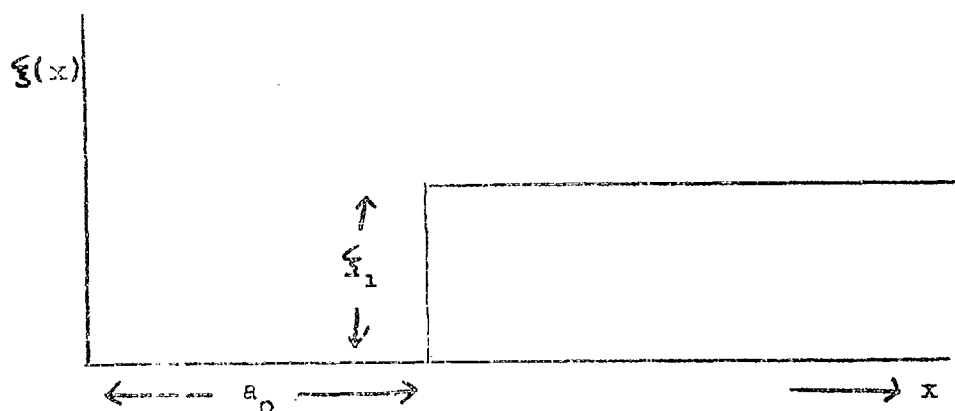
Case 1. Model for reaction rate $\xi(x)$.

Figure 3

f is just the fraction of n capable of reacting.

$$f = \int_{a_0}^{x_0} \frac{dx}{\pi \sqrt{x_0^2 - x^2}} = \frac{1}{\pi} \left[\sin^{-1} \frac{x}{x_0} \right]_{a_0}^{x_0} = \frac{1}{\pi} \left[\frac{\pi}{2} - \sin^{-1} \frac{a_0}{x_0} \right]$$

so that

$$K_1 = 0 \qquad \text{if } x_0 < a_0$$

$$K_1 = \frac{\xi}{\pi} \left[\frac{\pi}{2} - \sin^{-1} \frac{a_0}{x_0} \right] \qquad \text{if } x_0 > a_0 \tag{6}$$

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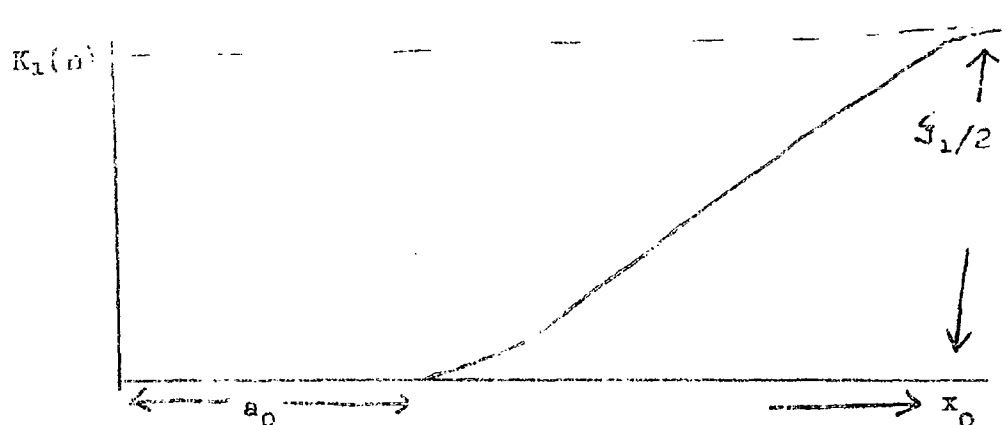
Case 1. $K_1(n)$ as a function of amplitude x_0.

Figure 4

2. In some cases one may expect the reaction rate $\mathcal{F}$ to be a delta function as shown in Figure 5.
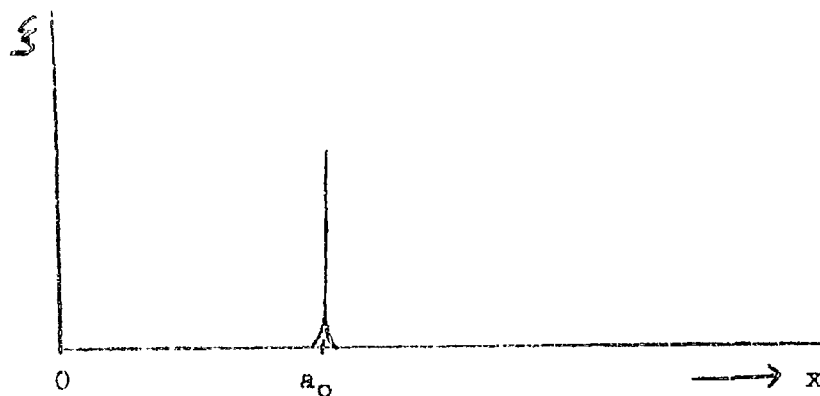
Case 2. $\mathcal{F}(x)$ a delta function at $x = a_0$.

Figure 5

That is,

$$\mathcal{F} = \mathcal{F}_2 a_0 \delta(x - a_0) \tag{7}$$

a_0 is introduced so that $\mathcal{F}_2$ may be of the same dimension as $\mathcal{F}_1$. In this case we denote the effective reaction rate constant by K_2.

One obtains from equation (3) again

$$K_2 = \int_{-x_0}^{x_0} P \mathscr{F}_2 a_0 \delta(x-a_0) d\tau = \frac{\mathscr{F}_2 a_0}{\pi} \int_{-x_0}^{x_0} \frac{\delta(x-a_0) dx}{\sqrt{x_0^2-x^2}}$$

Integrating this, one has for the effective reaction rate K_2

$$K_2 = 0 \qquad\qquad \text{if } x_0 < a_0$$

$$K_2 = \frac{\mathscr{F}_2}{\pi} \frac{a_0}{\sqrt{x_0^2-a_0^2}} \qquad \text{if } x_0 > a_0 \qquad (8)$$

A qualitative plot of K_2 as a function of amplitude x_0 is shown in Figure 6.
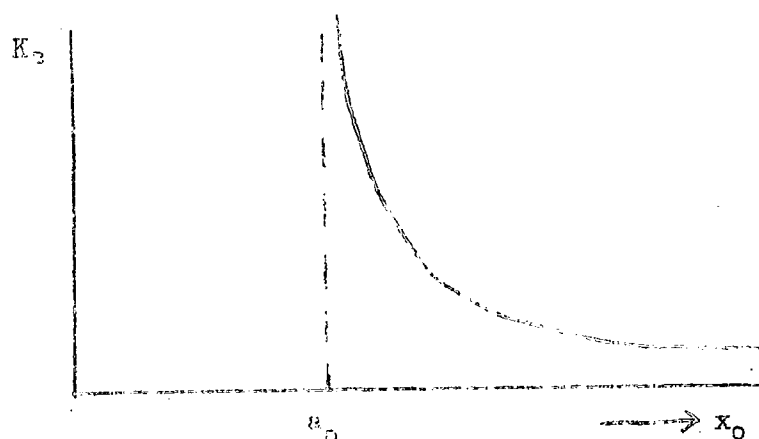
Case 2. K_2 as a function of the amplitude x_0.

Figure 6

3. There can be a case such that the reaction probability is a linear function of the velocity and occurs when $x = a_0$, so that it is given by the operator

$$\mathscr{F}(x) = \mathscr{F}_2 T \delta(x-a_0) v \qquad (9)$$

where T is the period of oscillation and v the velocity of x_0.

The rate constant is then

$$K_3 = \mathcal{F}_3 T \int_{-x_0}^{x_0} P\delta(x-a_0)v\,dx = \mathcal{F}_3 T \int_{-x_0}^{x_0} \frac{\delta(x-a_0)}{\pi \sqrt{(x_0^2-x^2)}} \omega \sqrt{x_0^2-x^2}\,dx$$

$$= \mathcal{F}_3 T \frac{\omega}{\pi} = 2\mathcal{F}_3$$

Thus,

$$K_3 = 0 \qquad \text{if } x_0 < a_0$$

$$K_3 = 2\mathcal{F}_3 \qquad \text{if } x_0 > a_0 \tag{10}$$

In this case effective reaction rate is simply a constant when the amplitude exceeds a_0. Plot of K_3 as a function of x_0, then is simply as shown in Figure 7.
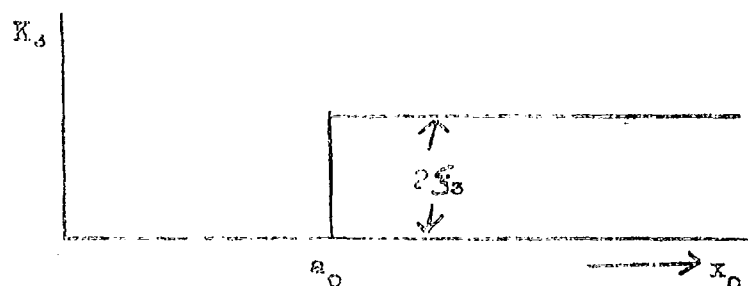
Case 3 K_3 as a function of the amplitude x_0.

Figure 7

Section II.   Einstein Approximation.

In order to obtain the overall reaction rate, that is, the total number of reactions per second per unit mass of a solid which is in a thermal equilibrium, it is

now necessary to calculate distribution of amplitudes x_0 at a given temperature.

In the Einstein approximation we regard the crystal as consisting of N independent oscillators, all of which are vibrating with the common circular frequency ω. If we assume that the oscillators are harmonic the energy is

$$E = \frac{1}{2}m\omega^2 x_0^2 \qquad (11)$$

which is, in quantum mechanics, $n\hbar\omega$ where n is the quantum number and may take on positive integer values. Thus

$$x_0 = \sqrt{\frac{2n\hbar}{m\omega}} \qquad (12)$$

The probability of finding an oscillator in the quantum state n is given by

$$\frac{e^{-n\hbar\omega/kT}}{1-e^{-\hbar\omega/kT}} \qquad (13)$$

Einstein was able to account for the essential behavior of the heat capacity of crystal by this model. By means of this model one can now calculate an average reaction rate.

The number of reactions which occur in unit time per cm^3 is then given by

$$K = \int_0^{n\infty} K(n)\frac{e^{-n\hbar\omega/kT}}{1-e^{-\hbar\omega/kT}}dn \qquad (14)$$

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where $K(n)$ is the effective reaction rate calculated in the previous section expressed as a function of the quantum number n. By using three expressions for K obtained before we can perform the above calculation as follows:

Case 1

$$\bar{K} = \int_0^\infty \frac{K_1(n)e^{-n\hbar\omega/kT}}{1-e^{-\hbar\omega/kT}}\,dn$$

$$= \frac{S_1}{n(1-e^{-\theta/T})} \int_{n_0}^\infty \left[\frac{1}{2} - \sin^{-1}\frac{a_0}{x_0}\right] e^{-n\theta/T}\,dn, \quad (15)$$

where $\quad x_0^2 = \dfrac{2n\hbar}{m\omega}, \quad a_0^2 = \dfrac{2a_0\hbar}{m\omega}, \quad \dfrac{\hbar\omega}{k} = \theta$

Consider the portion of the integral in $\sin^{-1}\dfrac{a_0}{x_0}$.

$$\int_{n_0}^\infty \sin^{-1}\frac{a_0}{x_0} e^{-n\theta/T}\,dn = \int_{n_0}^\infty \sin^{-1}(n_0/n)^{\frac{1}{2}} e^{-\theta n/T}\,dn$$

The exponential is a maximum at $n = n_0$ and decreases very rapidly as n increases. Therefore an accurate expansion for $\sin^{-1}(n_0/n)^{\frac{1}{2}}$ is required only for $n \approx n_0 (\sin^{-1}n_0/n \approx \pi/2)$.

Now $\quad \sin(\pi/2 - y) \approx 1 - y^2/2$ so $\pi/2 - y = \sin^{-1}(1 - y^2/2)$

Let $\quad z = 1 - y^2/2, \quad y = \sqrt{2(1-z)}$, since $z \approx 1$, let $2 \approx 1+z$

Then $\qquad \pi/2 - (1-z^2)^{\frac{1}{2}} \approx \sin^{-1}z$

So that $\quad \sin^{-1}(n_0/n)^{\frac{1}{2}} \approx \pi/2 - (n-n_0)/n \approx \pi/2 - (n-n_0)/n_0$

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Thus

$$\int_{n_0}^{\infty} \sin^{-1}(n_0/n)^{\frac{1}{2}} \ e^{-\theta n/T} dn \approx \int_{n_0}^{\infty} \left[\pi/2 - \left(\frac{n-n_0}{n_0}\right)^{\frac{1}{2}} \right] e^{-\theta n/T} dn$$

So integral for $\bar{K}_1$ is

$$K_1 = \frac{\zeta_1}{\pi} \ \frac{1}{(1-e^{-\theta/T})} \ \frac{1}{(n_0)^{\frac{1}{2}}} \int_{n_0}^{\infty} (n-n_0)^{\frac{1}{2}} \ e^{-\theta n/T} dn$$

Let $\quad n - n_0 = N$

$$\int_{n_0}^{\infty} (n-n_0)^{\frac{1}{2}} \ e^{-\theta n/T} dn = e^{-\theta n_0/T} \int_{0}^{\infty} N^{\frac{1}{2}} e^{-\theta N/T} dN$$

Letting $N = x^2$, integral in N becomes

$$2 \int_{0}^{\infty} x^2 e^{-\theta x^2/T} dx = 2 \ \sqrt{\frac{\pi}{4}} \left(\frac{T}{\theta}\right)^{3/2}$$

Thus

$$\bar{K}_1 = \frac{\zeta_1}{2\sqrt{\pi n_0}} \ \frac{e^{-T_c/T}}{1-e^{-\theta/\theta}} \left(\frac{T}{\theta}\right)^{3/2} \tag{16}$$

Where

$$n_0 = \frac{r\,\omega^2 a_0^2}{2} \quad \text{and} \quad T_0 = \frac{\hbar\omega n_0}{k} = \frac{m\omega^2 a_0^2}{2k}$$

Case 2

$$\bar{K}_2 = \int_{0}^{\infty} K_2(n) \ \frac{e^{-n\hbar\omega/kT}}{1-e^{-\hbar\omega/kT}} dn$$

$$\bar{K}_2 = \frac{\zeta_3 a_0}{\pi} \int_{n_0}^{\infty} \frac{1}{\sqrt{\frac{2n\hbar}{m\omega} - a_0^2}} \ \frac{e^{-n\hbar\omega/kT}}{1-e^{-\hbar\omega/kT}} dn$$

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$$K_2 = \frac{\mathcal{G}_2 a_0}{\pi} \frac{1}{1-e^{-\hbar\omega/kT}} \frac{1}{\left(\frac{2\hbar}{m\omega}\right)^{\frac{1}{2}}} \int_{n_0}^{\infty} \frac{e^{-bn}}{\sqrt{n-n_0}}$$

where $n_0 = \dfrac{a_0^2 m\omega}{2\hbar}$, $b = \dfrac{\hbar\omega}{kT}$

Consider the integral, $I = \displaystyle\int_{n_0}^{\infty} \frac{e^{-bn}}{n-n_0} dn$. Let $\nu = n-n_0$

$$I = \int_0^{\infty} e^{-b\nu} e^{-bn_0} d\nu,$$

Letting $\nu = \alpha^2$

$$I = 2e^{-bn_0} \int_0^{\infty} e^{-b\alpha^2} d\alpha = e^{-bn_0} \sqrt{\frac{\pi}{b}}$$

Thus

$$K_2 = \frac{\mathcal{G}_2 \sqrt{n_0}}{\sqrt{\pi}} \left(\frac{T}{\theta}\right)^{\frac{1}{2}} \frac{e^{-T_0/T}}{(1-e^{-\theta/T})} \tag{17}$$

Case 3

For K_3 the integral is simply

$$\bar{K}_3 = 2\mathcal{G}_3 \int_{n_0}^{\infty} \frac{e^{-n\hbar\omega/kT}}{1-e^{-\hbar\omega/kT}} dn$$

$$= - \frac{2kT\mathcal{G}_3}{\hbar\omega} \frac{1}{1-e^{-\hbar\omega/kT}} \left[e^{-n\hbar\omega/kT} \right]_{n_0}^{\infty}$$

$$K_3 = 2\mathcal{G}_3 \frac{T}{\theta} \frac{e^{-T_0/T}}{1-e^{-\theta/T}} \tag{18}$$

with the same expression for T_0 as before.

In order to compare the theoretical models with experimental results, it is necessary to know how K varies

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with T experimentally. The principal variation of K with temperature, of course, will occur via the Arrhenius factor because of the large values obtained for E_0 (of the order of 20-40 kilicalories per mole). The "activation temperature", that is, the quantity E_0/R will then vary between $10,000^\circ$ and $20,000^\circ$ Kelvin. At the time of this writing, we have not had an opportunity to examine all available experimental data on the reaction rate constants as a function of temperature in order to determine whether the smaller effect associated with the f(T) in the reaction rate constant $K = Af(T)e^{-E_0/RT}$ can be separated from the effect of the Arrhenius term $e^{-E_0/RT}$ (when R rather than K appears in the exponential, it is understood that E_0 is then expressed in calories per mole). Careful study of experimental data should be carried out. A brief discussion relating to some experimental results for NH_4NO_3 will be presented in a later section.

There are experimental situations other than a direct determination of K, however, which may enable one to say something about the applicability of f(T) to the explanation of experimental results. Reaction rate constant appears in the general conservation of heat equation

$$C\rho\frac{\partial T}{\partial t} = \lambda\nabla^2 T + QnK$$

where C is the specific heat, ρ is the density, λ is the thermal conductivity, Q the heat of reaction per mole, n the number of moles per unit volume, and K the calculated reaction rate constant. To reduce the

complexity of this equation and also to define a simple experimental arrangement, one may investigate solutions for either an adiabatic arrangement or for a steady state condition.

The stationary state is defined by

$$\lambda \nabla^2 T = Qn\bar{K}$$

Explosion takes place when this equation is not satisfied, that is, when a stationary state cannot exist. Frank-Kamenetski [Acta Phys. Chem. URSS 10, 365 (1939)] considered this type of problem with

$$\bar{K} = A \exp(-E/kT)$$

where A is a temperature independent factor. We shall investigate the effect of the temperature dependence of A as given by the three models.

A very simple experimental arrangement, which in principal should be subject to exact mathematical description, is one in which a sample of the explosive is placed in a temperature controlled bath or environment. Both the explosive and the bath start out at the same temperature. Because of internal reactions, however, the explosive will generate heat internally and its temperature will rise. One may then adjust the temperature of the surrounding bath so that its temperature rises simultaneously. In this way no heat is lost from the explosive. That is, the term $\lambda \nabla^2 T$ is equal to 0 and the reaction takes place under

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adiabatic condition.   The heat flow equation to be
solved then is simply

$$c \rho \frac{\partial T}{\partial t} = QnK$$

In this case the equation can be integrated and the
temperature of the explosive determined as a function of
time up to detonation. The $f(T)$ term in K will yield
somewhat different results depending on the form of $f(T)$.
One may then attempt to compare these theoretical results
with experimental curves to determine the importance of
$f(T)$.

At the time of this writing we have not been able
to find experimental data for this type of adiabatic
experiment. However, some theoretical curves have been
calculated and the results will be presented in the
next section.

Steady State Theory

In the Frank-Kamenetski theory explosion takes
place for those values of r and T for which the following
equation is satisfied:

$$\eta = \frac{QNr^2}{\lambda} \, g(T) \, e^{-E/kT}$$

where $E = a_0^2 M \omega^2 / 2$

η is a constant which depends on the geometrical shape of
the explosive, r is the linear dimension of it, N is the
number of reacting molecules per unit volume, Q is the
heat of reaction and λ is the thermal conductivity. In
the Frank-Kamenetski case:

$$g(T) = \frac{AE}{kT^2} = \frac{AT_0}{T^2}$$

In our Case 1:

$$g(T) = \frac{\mathfrak{z}_1}{2\sqrt{\pi n_0}} \frac{T_0}{\theta^{3/2}(1-e^{-\theta/T})T^{\frac{1}{2}}}$$

In our Case 2:

$$g(T) = \frac{\mathfrak{z}_2\sqrt{n_0}}{\sqrt{\pi\theta}} \frac{T_0}{(1-e^{-\theta/T})T^{3/2}}$$

In our Case 3:

$$g(T) = \frac{(2n_0)^{\frac{1}{2}}\mathfrak{z}_3 T_0}{\pi\theta(1-e^{-\theta/T})T}$$

The difference among these four cases appears
when the explosive material becomes very small. We

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notice that in the Frank-Kamenetski case there exists an
absolute critical radius such that below that radius
explosion can never take place even at high temperature.
The critical radius is obtained by solving for r_{min} in
the Frank-Kamenetski relationship

$$\eta = \frac{\alpha r^2}{T^2} e^{-T_0/T}$$

where $\qquad T_0 = \frac{E}{k}, \quad \alpha = \frac{QnAE}{\lambda k}$

which can be written as

$$r^2 = \frac{\eta T^2}{\alpha} e^{T_0/T}$$

for the critical radius.

Thus for Frank-Kamenetski case, the absolute critical
radius is

$$r_c = \frac{e}{2} \sqrt{\frac{\lambda \eta E}{QNAk}}$$

where e is the exponential, and the corresponding
temperature is

$$T_c = T_0/2$$

As can be seen from the general expression for r^2,
an appreciable change of the critical radius r appears
when T becomes comparable to T_0. By looking at a curve
we can say that such change of r with T occurs at about

$T = T_0/2.5$. If we take this criterion we see from the formula for r^2 that the critical radius at such temperature is about $1.1\ r_c$, which means if the change of explosion temperature is observable, the absolute critical temperature is also observable.

In our cases one can obtain the absolute critical radius in the same way, and one may verify that they occur at

$$T_c = 2(T_0 + \theta) \qquad \text{for Case 1}$$

$$T_c = \frac{2}{3}(T_0 + \theta) \qquad \text{for Case 2}$$

$$T_c = T_0 + \theta \qquad \text{for Case 3}$$

Since the T-dependence of the critical radius is determined primarily by the exponential function $e^{T_0/T}$, the above criterion $T = T_0/2.5$ in order to have an appreciable change of r with temperature may be applied in all of the above cases also. Thus the radius at which the explosion temperature changes are approximately

$$1.9\ r_c \qquad \text{for Case 1}$$

$$1.1\ r_c \qquad \text{for Case 2}$$

$$1.4\ r_c \qquad \text{for Case 3}$$

Experimental results[1] show a change of explosion temperature with the dimension of explosive. However, there is no definite result for the absolute critical radius. Thus our Case 1 is favorable over other cases including the original Frank-Kamenetski case.

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1. F. P. Bowden and A. C. McLaren, cited in p. 30 of Bowden and Yoffe's "Fast Reactions in Solids", 1958.

Adiabatic Reactions

The Adiabatic Heat Balance Equation is

$$C\frac{dT}{dt} = Q\overline{K}$$

where C = heat capacity/mole

Q = heat of decomposition/mole

For the three functions, $\mathcal{f}(x)$, considered in Section I, $\overline{K}$ will be of the form

$$\overline{K} = Af(T)e^{-T_0/T}$$

where

$$f(T) = \frac{T^n}{1-e^{-\theta/T}}$$

and A involves the constants which vary with the particular model. For the present we shall regard A as determined from experimental data for a particular substance. That is, no attempt will be made to evaluate A from more fundamental properties of the solid.

The heat balance equation becomes

$$\int_{T_1}^{T} \frac{e^{T_0/T}}{f(T)}dT = \int_{t_1}^{t} \frac{AQ}{C}dt$$

Since $f(T)$ is a slowly varying function compared with $e^{T_0/T}$, we shall, at present, carry out the integration in T by treating $f(T)$ as constant. Thus one obtains

$$\frac{AQ}{C}(t-t_1) = \left[\frac{T_1^2}{f(T_1)T_0}e^{T_0/T_1} - \frac{T^2}{f(T)T_0}e^{T_0/T} \right]$$

Thus, for each of the three cases one obtains the
results:

Case 1

$$t-t_1 = \frac{C}{QA_1T_o}\left[T_1^{\frac{1}{2}}(1-e^{-\theta/T_1})\,e^{T_o/T_1} - T^{\frac{1}{2}}(1-e^{-\theta/T})e^{T_o/T}\right]$$

$$A_1 = \frac{\mathcal{F}_1}{2(\pi n_o)^{\frac{1}{2}}\theta^{3/2}}$$

Case 2

$$t-t_1 = \frac{C}{QA_2T_o}\left[T_1^{3/2}(1-e^{-\theta/T_1})e^{T_o/T_1} - T^{3/2}(1-e^{-\theta/T})e^{T_o/T}\right]$$

$$A_2 = \frac{\mathcal{F}_2 n_o^{\frac{1}{2}}}{(\pi\theta)^{\frac{1}{2}}}$$

Case 3

$$t-t_1 = \frac{C}{QA_3T_o}\left[T_1(1-e^{-\theta/T_1})e^{T_o/T_1} - T(1-e^{-\theta/T})e^{T_o/T}\right]$$

$$A_3 = \frac{\mathcal{F}_3(2n_o)^{\frac{1}{2}}}{\theta\pi}$$

When the Arrhenius equation, $\bar{K} = Ae^{-T_o/T}$ is used
for $\bar{K}$, the result is

$$t-t_1 = \frac{C}{AQT_o}\left[T_1^2 e^{T_o/T_1} - T^2 e^{T_o/T}\right]$$

When the Eyring form, $\bar{K} = A'Te^{-T_o/T}$ is used, one
obtains

$$t-t_1 = \frac{C}{A'QT_o}\left[T_1 e^{T_o/T_1} - T_3^{T_o/T}\right]$$

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The following calculation is an exploratory one to determine the nature of the temperature versus time curve for the adiabatic decomposition of a typical explosive. In the calculation it is assumed that an initial reaction rate constant is known [2]. It will be assumed that the reaction rate constant is a function only of the temperature and not of the time. One may arbitrarily take the Arrhenius value of A for EDNA which according to Cook[2] is $10^{11.1}$. We will assume that this value of A is determined from the experimental isothermal reaction rate constant at a temperature of $427^{\circ}K$. The constant in our case1, which we will call A'', is then given by

$$A'' = A(1-e^{-\theta/T'})/T'^{3/2}$$

where T' is the temperature at which A is determined, in this case $427^{\circ}K$. One may then assume an adiabatic reaction starting from some arbitrary initial temperature, say $373^{\circ}K$, and carry the calculation to $433^{\circ}K$. Results of such a calculation are shown in Figure 8 for two arbitrarily selected values of the Einstein temperature $\theta = 200^{\circ}K$, $\theta = 800^{\circ}K$.

One may note that there is a 20-30 percent difference in the predicted time from reaction initiation to

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2. "Isothermal Decomposition of Explosives" by M. A. Cook and M. Taylor Abegg, Industrial and Engineering Chemistry, 48, p. 1090, June 1956.

An absolute temperature versus time for adiabatic decomposition of a typical explosive (Arrhenius frequency factor equal to $10^{11.1}$).

Figure 8

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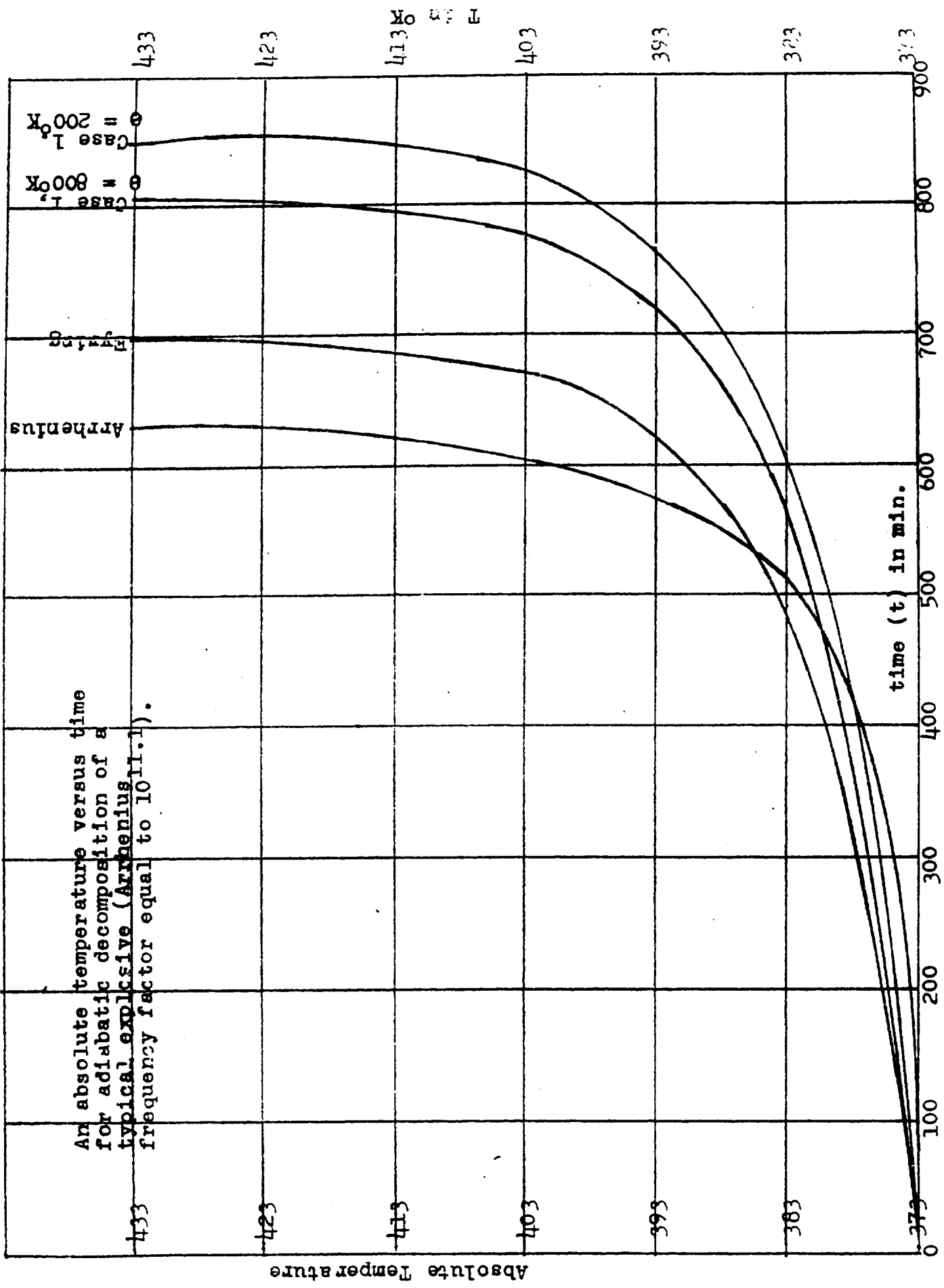
detonation using the Arrhenius reaction rate constant and
using our Case 1 reaction rate constant. The adoption
of a reaction rate constant determined from an isothermal
experiment to describe the adiabatic reaction may be
open   to question but the curves do give one a qualitative
indication as to how the temperature time predictions will
behave for the various forms of the reaction rate constant.

Using the experimental data for log K(T) obtained
by Cook (see Ref. 2) for NH_4NO_3, an attempt was made to
determine whether our Case 1 would fit the K(T) curve more
accurately than the simple Arrhenius reaction rate constant.
It was found that no measureable improvement was obtained
by introducing the factor $T^{3/2}(1-e^{-\theta/T})$. Since the data
used in the calculation were taken directly from the
graphs of Ref. 2, it is possible this calculation may
be improved by referring to the original data.

Conclusions and Recommendations

The reaction rate theory developed in this chapter
predicts a higher function of the temperature in addition
to the usual Arrhenius factor in describing solid state
reaction rate constants. Predictions of the theory
therefore differ from those made on the basis of the
Arrhenius or Eyring theory.

It is recommended that further work be carried out
in order to develop improved models for the function $\mathcal{S}(x)$
defined in the text. Further applications also should be
made to reaction dependent phenomena.

Chapter III

PRELIMINARY CALCULATIONS RELATING TO EXPLOSION INDUCED BY A FALLING BODY

M. Mizushima

A shock wave can excite the lattice vibrations. If the maximum amplitude is x_0 the energy of an oscillator per atom is $\frac{1}{2}\omega^2 M x_0^2$. Thus in a simplified model which assumes that n oscillators are excited by the same amount gives the total energy as

$$W = \frac{n}{2}\omega^2 M x_0^2$$

The number n must be proportional to the duration time of the excitation divided by the velocity of the sound wave in the explosive. Suppose such shock wave is excited by a body which changes its momentum from p to zero during time Δt we have

$$M\ddot{x} = -kx = \frac{Ay}{\lambda}x$$

$$\omega^2 = \frac{Ay}{M\lambda}, \quad \frac{dp}{\Delta t} = F = \frac{1}{2}Nkx_0 = \frac{1}{2}NM\omega^2 x_0$$

$$T = 2\pi\sqrt{\frac{M\ell}{Ay}}$$

if $\qquad \omega\Delta t \ll 1$

If Δt is much larger than $1/\omega$, we have

$$\frac{dp}{\Delta t} = \frac{1}{\omega\Delta t}NM\omega^2 x_0 \quad \text{if } \omega\Delta t \gg 1$$

as discussed in the appendix.

One may define α as the fraction of momentum which is used to excite the shock wave in the explosive crystal. If the collision is perfectly elastic

$$\alpha = 0.$$

If it is completely inelastic

$$\alpha = \frac{m_2}{m_1 + m_2}$$

where m_1 and m_2 are masses of hitting body and body hitted, respectively. In our case α must be very small since the collision is nearly elastic.

The lattice wave propagates with the velocity of sound u. The number of excited oscillators, n, is thus

$$n = NAu\Delta t$$

where N is the number of oscillators in the unit volume and A is the area which is hit by the external body.

From the preceding equations, we have

$$\Delta t = (\alpha P/2NAuM\omega^2 x_0)^{\frac{1}{2}}$$

$$n = (\alpha PNAu/2M\omega^2 x_0)^{\frac{1}{2}}$$

if $\qquad \Delta t \ll 1/\omega$, and

$$\Delta t = \alpha P/NAuM\omega x_0$$

$$n = \alpha P/M\omega x_0$$

if $\qquad \Delta t \gg 1/\omega$

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For example, if the hitting body has the same density as the explosive and its velocity is v

$$\alpha P/2NAuMx_0 \longrightarrow \alpha(v/u)(\ell/2x_0)$$

where ℓ is the thickness of the hitting body. If v is 100 cm/sec, ℓ is 1 cm, the above ratio is about 10^4 since u is about 10^5 cm/sec, x_0 is about 10^{-7} cm. Thus if $\alpha \gg 10^{-4}$ we have a $\omega\Delta t \gg 1$ case, but if $\alpha \ll 10^{-4}$ it is a $\omega\Delta t \ll 1$ case.

If we drop a mass m from the height h the momentum p is

$$p = m(2gh)^{\frac{1}{2}}$$

thus

$$n = (\alpha m NAu/2M\omega^2 x_0)^{\frac{1}{2}}(2gh)^{1/4}$$

if $\omega\Delta t \ll 1$, and

$$n = (\alpha m/M\omega x_0)(2gh)^{\frac{1}{2}}$$

if $\omega\Delta t \gg 1$.

Now the energy of this hitting body is mgh, so that

$$W = \beta mgh$$

where β gives the fraction of the energy absorbed by the shock wave. It is expected that β is about 0.5. Using the above equations, one can obtain

$$x_0 = \gamma h^{\frac{1}{2}}$$

where

$$\gamma = \left(\frac{2\beta}{\omega}\right)^{2/3} \left(\frac{\alpha m}{MNAu}\right)^{1/3} g^{\frac{1}{2}}$$

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if $\omega \Delta t \ll 1$. If, on the other hand $\omega \Delta t \gg 1$,

$$\Upsilon = (\beta/\alpha\omega)(g/2)^{\frac{1}{4}}$$

if $\omega \Delta t \gg 1$.

We see easily that

$$\Delta t = 2^{-7/12}(\alpha m/\beta MNAu\omega^2)^{1/3}, \text{ if } \omega \Delta t \ll 1$$

$$\Delta t = 2\alpha^2 m/\beta MNAu, \qquad \text{if } \omega \Delta t \gg 1$$

Suppose h is 10 cm, we have $v = 100$ cm/sec which gives the previous example. Since ω is about 10^{12} sec^{-1}, α should be about $10^{-2.5}$ in order that x_0 is 10^{-7} cm. From the last equation above, we have Δt of about 10^{-10} sec. Thus we have a consistent picture of $\omega \Delta t \gg 1$ case here.

Using $x_0 = \Upsilon h^{\frac{1}{2}}$ we obtain the reaction rate K for three cases considered in the preceding chapter.

$$K_1 = \frac{3_L}{2\pi}\left[\frac{\pi}{2} - \sin^{-1}\left(\frac{h_0}{h}\right)^{\frac{1}{2}}\right] \qquad \text{if } h > h_0$$

$$= 0 \qquad \text{if } h < h_0$$

$$K_2 = \frac{\zeta_2}{2\pi}\frac{h_0}{(h-h_0)^{\frac{1}{2}}} \qquad \text{if } h > h_0$$

$$= 0 \qquad \text{if } h < h_0$$

$$K_3 = \zeta_3 \qquad \text{if } h > h_0$$

$$= 0 \qquad \text{if } h < h_0$$

where $h_0 = (a_0/\gamma)^2$

In Figure A the corresponding curves are shown.

Since the velocity of sound is independent of the amplitude the above quantity essentially gives the number of reactions per unit volume. Explosion will take place if the reaction per unit volume is above certain value so that the temperature of the explosive can be above the explosion temperature.

The number of reactions which take place in unit volume is

$$\int NK \Delta t$$

From our equations for Δt we see that Δt is independent of h in any case, the height dependence of the above number of reactions per unit volume is given by the K part, namely, by our equations for K_1, K_2, K_3 for three typical cases, respectively.

The explosion can occur if the temperature reaches to the explosion temperature T_e by these reactions. Assuming that we can neglect the heat conduction during Δt the condition of explosion is

$$\frac{\theta}{C} NK \Delta t \geq T_e - T$$

where θ is the heat produced by each reaction, C is the specific heat, T is the original temperature.

For a given size of the explosive the explosion temperature T_e is given as discussed in the preceding chapter.

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The above formula gives the minimum original temperature T necessary for explosion as a function of the height h if we put out various expressions for K and for Δt into it. The result can be seen in Figure B. These three cases can be easily distinguished from each other in this case. Such experiment will thus be a good test to see which assumption is correct.

Conclusions and Recommendations

The reaction rate theory developed in this text may be applied to the description of explosion initiation by a falling body.

A preliminary and simplified treatment given herein should be amplified so as to include further detail.
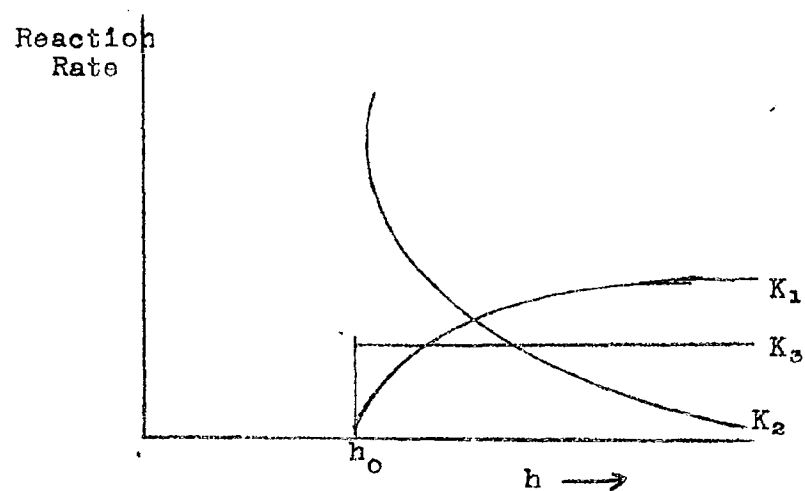
Figure A. Reaction rate as a function
of height for cases 1, 2, 3.
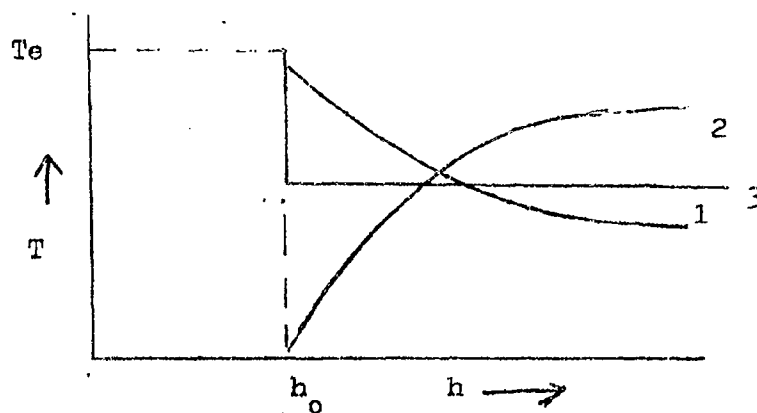
Figure B. Minimum original temperature
necessary for explosion as a
function of height. Curves 1,
2, 3 correspond to our cases
1, 3, and 3, respectively.

Appendix

CALCULATION OF THE FORCE DUE TO SHOCK WAVE

We suppose a linear chain made by single kind of atoms combined together with force constant $m\omega^2$. If we hit one end of this chain the vibration of this atomic system, which is nothing but a longitudinal sound wave or lattice wave, will be excited at that end. The wave will propagate with the sound velocity u and the inter-atomic distance r at distance y measured from the end will experience a displacement x from its equilibrium value r_0 as

$$x = x_0 \cos \omega(\frac{y}{u} - t)$$

If the excitation mechanism is such that it keeps pro-ducing such lattice wave at the end in the same way
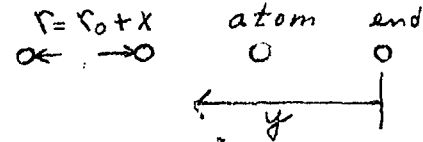
Figure 1, Linear chain.

throughout a period Δt, we will have a region from the end surface to depth $y = ut$ in which all atoms are excited and interatomic distances given by the above formula, but beyond that region no excitation.

$$x = x_0 \cos \omega(\frac{y}{u} - t) \qquad \text{for } y \leqslant ut$$
$$x = 0 \qquad \text{for } y > ut$$

The total displacement, namely the change of the length of this chain, at time t smaller than Δt will be given by integrating the following expression. Using notation N for the number of atoms in unit volume and n for the total number of excited atoms after the time interval Δt, we obtain the following result, since

$$n = NAu\Delta t$$

The total displacement at t is

$$x = NA \int_0^{ut} x \, dy = NA \, x_0 \int^{ut} \cos\omega(\frac{y}{u} - t) \, dy$$

$$= nx_0 \frac{\sin \omega t}{\omega \Delta t}$$

The total force due to the displacement is

$$F = nM\omega^2 x_0 \frac{\sin \omega t}{\omega \Delta t}$$

The above total displacement x can be both positive and negative. If the impact is so strong that the surface cannot be pushed back, the negative value of x cannot exist. We assume that each time x tries to be negative a new wave is generated at the surface so that x always stays positive. One such wave is

$$x = nx_0 \frac{|\sin \omega t|}{\omega \Delta t}$$

for example. In this case we have

$$F = nM\omega^2 x_0 \frac{|\sin \omega t|}{\omega \Delta t}$$

The average total force over the duration time Δt is

$$\langle F \rangle_{AV} = \frac{\int_{0}^{\Delta t} F \, dt}{\Delta t}$$

If $\omega \Delta t \ll 1$ we have for both cases, that is for $F \sim \sin \omega t$ and $F \sim |\sin \omega t|$

$$\langle F \rangle_{AV} = \frac{n}{2} M \omega^2 x_0$$

while if $\omega \Delta t \gg 1$ we have

$$\langle F \rangle_{AV} = n M \omega^2 x_0 \, \frac{1 - \cos \omega \Delta t}{(\omega \Delta t)^2} \simeq \frac{n M \omega^2 x_0}{(\omega \Delta t)^2}$$

for the $\sin \omega t$ case and

$$\langle F \rangle_{AV} \simeq \frac{2}{\pi} \frac{n M \omega^2 x_0}{\omega \Delta t} \simeq \frac{n M \omega^2 x_0}{\omega \Delta t}$$

in the case of $|\sin \omega t|$.

If we take F for the $\sin \omega t$ case, we obtain

$$P = N A u M x_0$$

which means x_0 is about 10^{-4} cm under ordinary experimental setup. Obviously x_0 must be about 10^{-7} cm in our picture. Therefore, we do not take $\langle F \rangle$ corresponding to $F \sim \sin \omega t$ in this article but take $\langle F \rangle$ corresponding to $F \sim \sin \omega t$ instead.

THEORY OF DIELECTRIC CONSTANT AND
LOSS TANGENT FOR A MEDIUM CONTAINING IMPURITIES

Donald G. Burkhard

In the final report for Contract DA-44-009-ENG-3628, 1959 we reviewed various atomic and molecular mechanisms which give rise to a frequency dependent dielectric constant and loss tangent.

In the same report we calculated the frequency dependent dielectric constant and loss tangent for a medium containing impurity centers. The principal motivation for investigating this situation lies in the fact that newly formed "pure" lead azide decomposes with time. Therefore, if dielectric and loss tangent measurements are made on a specimen at different times, one is not necessarily dealing with a pure homogeneous specimen. When attempting to interpret microwave measurements, it is therefore of importance to know what type of frequency dependent behavior to expect as a result of the presence of impurities. The measured spectrum will, in addition to the impurity effect, have superimposed on it the characteristics of the molecular polarization associated with the pure medium and with the impurity centers. These effects may be incorporated into our general formulas for particular cases.

As we shall see in the next section, the exact calculation of the dielectric properties of an impure medium is analytically rather complicated. One may

substantially simplify the calculation, however, by using Lorentz's procedure for calculating the dielectric properties of a medium containing polarizable atoms and/or molecules. The procedure, as is well known, is to remove an imaginary sphere from the medium. The field at the center of the sphere and associated with the matter outside of the sphere is then computed by calculating the field associated with the polarization of the sphere. To obtain the total effective field at the center of the sphere one then replaces the matter in the sphere and calculates the local field associated with the individual charges of the matter in the sphere. Knowing the total effective field at an atom site, one may then express the atomic polarizability in terms of the external field and finally obtain an expression for the complex dielectric constant of the medium.

In a similar manner, the Lorentz sphere procedure was used to calculate the effective dielectric properties of a medium containing a cubical array of impurity centers. A requirement for accuracy of the calculation, however, is that the separation of impurity spheres be appreciably greater than their diameters. It is not clear just what the limits of accuracy of this model are. It was therefore considered desirable to attempt to solve the problem exactly by solving Laplace's equation for a

homogeneous medium containing a cubic array of dielectric spheres. It was found, after developing the above described Lorentz-type treatment that Rayleigh had calculated the effective conductivity of a medium containing a cubic array of conducting spheres. In this report we generalize Rayleigh's results in order to calculate the complex dielectric behavior of such a medium. The more exact but also more complicated results obtained by using Rayleigh's procedure are then compared with ours in order to determine the range of applicability of the latter. That is, we compare with the more accurate treatment in order to determine the maximum ratio of diameter of impurity to separation of impurity in order for our simplified procedure to yield accurate results.

We now summarize the procedure for calculating the complex dielectric constant for a homogeneous medium containing a cubic array of dielectric impurities. This will be done first by following Lorentz's procedure and will then be carried out by generalizing Rayleigh's method. In a later section, the effective dielectric constant and loss tangent for a compound medium will be shown graphically as a function of frequency for various percentages of "impurity" constant and for various values of the dielectric constant and loss tangent for the medium and for the impurities.

Allow the supporting medium to play the role of free space. That is, the supporting medium will be described by the dielectric constant

$$\varepsilon_o'^* = \varepsilon_o K_o^* = \varepsilon_o (K_o' - \frac{j\sigma_o}{\omega\varepsilon_o})$$

$$= [\varepsilon_o' - \frac{j\sigma_o}{\omega}]$$

We now treat the imbedded spheres as "atoms" in the supporting medium.

The Lorentz sphere is shown dotted in Figure 1. If the imbedded spheres form a cubic or random array of dipoles parallel to the field then the internal field of the spheres produces no effect. In this picture we now want to correlate ε_e' and σ_e for the composite medium with the macroscopic properties of the spheres and the supporting medium. The atomic polarization effects usually put into the Clausius-Mosotti equation now are those associated with the imbedded spheres. The three basic equations which lead to the Clausius-Mosotti equation are now

$$P = \varepsilon_o'^* \chi_e^* E_o$$

$$P = n_o \varepsilon_o'^* \alpha E_{eff}$$

$$E_{eff} = E_o + \frac{P}{3\varepsilon_o'^*}$$

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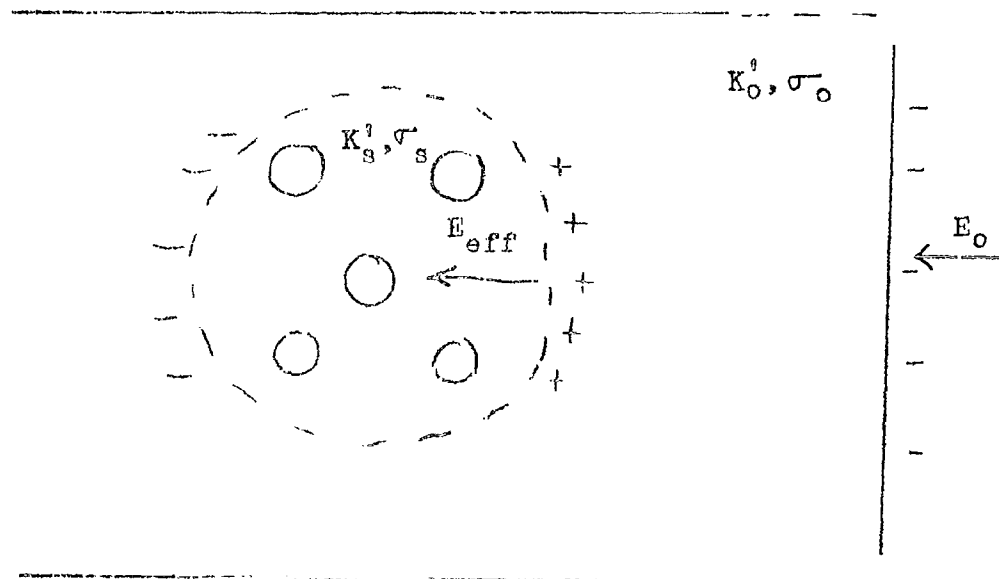
Figure 1. Imbedded spheres $K^*_s(K'_s, \sigma_s)$ in dielectric $K^*_o(K'_o, \sigma_o)$. Dotted line shows Lorentz sphere.

χ_e^* being the effective χ of the overall medium is then the χ of a medium consisting of the imbedded dielectric spheres in the "space" of the supporting medium. σ is the polarizability of the individual spheres in the supporting medium. The above equations yield the Clausius-Mossotti result

$$\chi_e^* = \frac{n\sigma}{1 - n\ \sigma/3}$$

$$\chi_e^* = K_e^* - 1$$

$$K_e^* = \frac{\varepsilon_e^*}{\varepsilon_o^{'*}}$$

Thus
$$\varepsilon_e^* = \varepsilon_o^{'*} \left(1 + \frac{n\sigma}{1 - n\ \sigma/3}\right)$$

$$(\omega\varepsilon_e^{''} - j\sigma_e^{'}) = (\omega\varepsilon_o - j\sigma_o^{'}) \left(1 + \frac{n\sigma}{1 - n\ \sigma/3}\right)$$

$$(\sigma_e^{''} + j\omega\varepsilon_e^{'}) = (\sigma_o^{''} + j\omega\varepsilon_o^{''}) \left(1 + \frac{n\sigma}{1 - n\ \sigma/3}\right)$$

or

$$\frac{\sigma_e}{\varepsilon_o} + j\omega K_e = \left(\frac{\sigma_o}{\varepsilon_o} + j\omega K_o\right) \frac{1 + 2/3\ n_o\sigma}{1 - n_o\ \sigma/3}$$

To calculate σ one must calculate the dipole moment associated with one of the imbedded spheres. This is

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done by solving for the potential outside of a conducting sphere in an infinite conducting dielectric medium.

The potential is[*]

$$\varphi_0 = \left(\frac{\varepsilon_s^* - \varepsilon_0^*}{2\varepsilon_0 + \varepsilon_s^*} \frac{a^3}{r^3} \right) \cdot E_{eff} z$$

First term contributes a potential which is the same as that of a dipole

$$p = \frac{\varepsilon_s^* - \varepsilon_0^*}{2\varepsilon_0^* + \varepsilon_s^*} a^3 E_0$$

where

$$\varepsilon_s^* = \varepsilon_s' - j\sigma_s/\omega = -j/\omega \, (\sigma_s - j\omega\varepsilon_s') = -\frac{j\varepsilon_0}{\omega} \left(\frac{\sigma_0}{\varepsilon_0} + j\omega K_0 \right)$$

$$\varepsilon_0^* = \varepsilon_0' - j\sigma_0/\omega = -j/\omega \, (\sigma_0 - j\omega\varepsilon_0') = -\frac{j\varepsilon_0}{\omega} \left(\frac{\sigma_s}{\varepsilon_0} + j\omega K_s \right)$$

$$\varepsilon_s' = \varepsilon_0 K_s$$

$$\varepsilon_0' = \varepsilon_0 K_0$$

where K_s and K_0 are the dielectric constants for the sphere and the medium, respectively. ε_0 is a constant, $10^7/4\pi C^2$, in MKS units; C is the velocity of light in free space in meters per second.

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[*] Chapter: "Theory of the Dielectric Constant" by D. G. Burkhard in Final Report, Contract DA-44-009-ENG-3628, July 1959.

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ϵ_s^*/ϵ_0 and ϵ_0^*/ϵ_0 are the complex dielectric constants for sphere and medium. The coefficient of E_0 is then the polarizability "σ" of our macroscopic spheres.

$$\sigma = p = \frac{1 - \epsilon_0^*/\epsilon_s^*}{1 + 2\,\epsilon_0^*/\epsilon_s}\, a^3$$

Putting the expressions for ϵ_0^* and ϵ_s^* in the equation for σ and letting

$$\sigma = \frac{1}{\epsilon_0}\,(\sigma_s + 2\sigma_0),\; \sigma' = \frac{1}{\epsilon_0}\,(\sigma_s - \sigma_0)$$

$$K = K_s + 2K_0 \quad \text{and} \quad K' = K_s - K_0 \, ,$$

one obtains:

$$\sigma = \frac{\sigma'' + j\omega K'}{\sigma'' + j\omega K}\, a^3$$

If we now put this expression for σ in the Clausius-Mosotti equation, one has:

$$\frac{\sigma_e}{\epsilon_0} + j\omega K_e = \left(\frac{\sigma_0}{\epsilon_0} + j\omega K_0\right)\frac{\sigma'' + (2/3)\sigma'' B + j\omega[K + (2/3)K'B]}{\sigma'' - (1/3)\sigma'' B + j\omega[K - (1/3)K'B]}$$

where $B = na^3 = \frac{3}{4\pi}\,nv$. v is the volume of a single impurity sphere and n is the number of such spheres per unit volume. If one now equates real and imaginary parts the following expressions are obtained for the effective dielectric constant, K_e, and conductivity σ_e,

of the composite medium

$$K_e =$$

$$\frac{K_0[(\sigma^2+\omega^2K^2)+\frac{1}{3}(\sigma\sigma'+\omega^2KK')B-\frac{2}{9}(\sigma'^2+\omega^2K'^2)B^2]+\frac{\sigma_0}{\varepsilon_0}(\sigma K'-\sigma'K)}{\sigma^2 + \omega^2K^2 - \frac{2}{3}(\sigma\sigma' + \omega^2KK')B+ \frac{1}{9}(\sigma'^2 + \omega^2K'^2)B^2}$$

$$\frac{\sigma_e}{\varepsilon_0} = \frac{\frac{\sigma_0}{\varepsilon_0}[(\sigma^2+\omega^2K^2)+\frac{1}{3}(\sigma\sigma'+\omega^2KK')B-\frac{2}{9}(\sigma'^2+\omega^2K'^2)B^2]-\omega^2K_0(\sigma K'-\sigma'K)B}{\sigma^2 + \omega^2K^2 - \frac{2}{3}(\sigma\sigma'+ \omega^2KK')B + \frac{1}{9}(\sigma'^2 + \omega^2K'^2)B^2}$$

In the above equations one now has K_e and σ_e expressed
in terms of K_0, σ_0, K_s, σ_s, B, ω:

$$K_0 = K_e(K_0, \sigma_0, K_s, \sigma_s, B, \omega)$$

$$\sigma_0 = \sigma_e(K_0, \sigma_0, K_s, \sigma_s, B, \omega)$$

Rayleigh Procedure

Following is a generalization of Rayleigh's procedure.[1]
In principle, there is no restriction on the size of the
impurity spheres. The results, however, are expressed
in terms of a series expansion so that one must be careful
to carry a sufficient number of terms for adequate
convergence.

1. Philosophical Magazine, Vol. 33-34 (1892) pp. 481-502.

Consider the medium as divided into an array of
rectangular units of dimensions α, β, and γ in the x, y,
and z directions, respectively.   See Figure 2
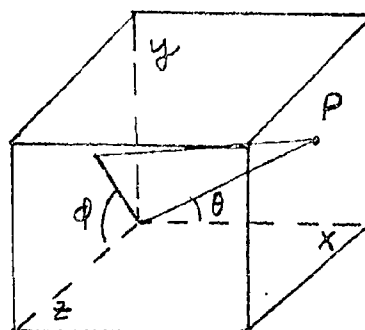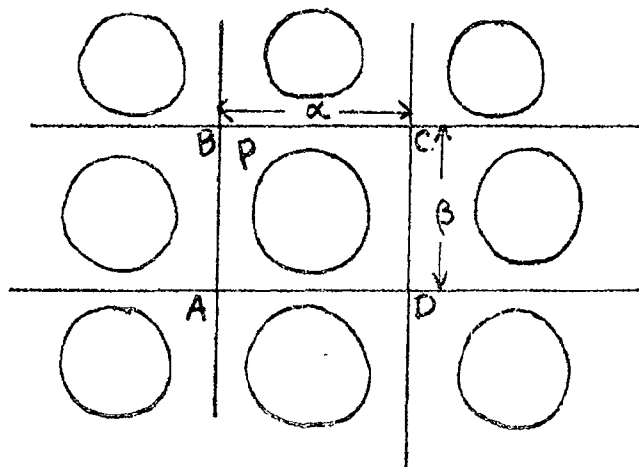
Figure 2

If one takes the center of one of the cylinders P as
origin of polar coordinates, the potential external to the

cylinder may be expanded in the series

outside $V = A_0 + (A_1 r + B_1 r^{-2}) Y_1 + \cdots + (A_n r^n + B_n r^{-n-1}) Y_n + \cdots$

inside $V' = C_0 + C_1 Y_1 r + \cdots + C_n Y_n r^n + \cdots$

Y_n denotes the spherical surface harmonic of order n. Boundary conditions on the surface of the sphere where $r = a$ are:

$$V = V', \qquad \nu \frac{dV'}{dn} = \frac{dV}{dn}$$

ν denotes the ratio of the complex dielectric constant of the sphere to the complex dielectric constant of the medium.

$$\nu = \frac{K_s^*}{K_o^*}$$

To apply boundary conditions, one has

$$\frac{dV}{dn} = (A_1 - \frac{2B_1}{r^3}) Y_1 + \cdots + n A_n r^{n-1} - \frac{(n+1)}{r^{n+2}} B_n Y_n + \cdots$$

$$\nu \frac{dV'}{dn} = \nu C Y_1 + \cdots \nu n C_n Y_n r^{n-1} + \cdots$$

Equating coefficients of the Y's for $r = a$

$$A_1 - \frac{2B}{a^3} = \nu C_1$$

$$A_n - \frac{(n+1) B_n}{n a^{2n+1}} = \nu C_n$$

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Likewise from $V = V^\parallel$

$$A_1 + \frac{B_1}{a^3} = C_1$$

$$\vdots \qquad \vdots$$

$$A_n + \frac{B_n}{a^{2n+1}} = C_n$$

From which

$$B_n = \frac{1- \nu}{1+\nu+1/n} \, a^{2n+1} \, A_n$$

We must now consider the limitations to be imposed upon Y_n. In general,

$$Y_n = \sum_{s=0}^{s=n} \Theta_n^\omega (H_s \cos s\varphi + K_s \sin s\varphi), \quad \cdots$$

where

$$\Theta_n^s = \sin^s\theta(\cos^{n-s}\theta - \frac{(n-s)(n-s-1)}{2(2n-1)} \cos^{n-s-2}\theta + \cdots)$$

θ being supposed to be measured from the axis of x (parallel to σ) and φ from the plane of xz. In the present application symmetry requires that s should be even, and that Y_n (except when $n = 0$) should be reversed when $(\pi-\theta)$ is written for θ. Hence even values of n are to be excluded altogether. Further, no sines of $s\varphi$ are

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admissible. Thus we may take

$$Y_1 = \cos\theta, \ \circ\circ\circ\circ\bullet\bullet\circ\circ$$

$$Y_3 = \cos^3\theta - \frac{3}{5}\cos\theta + H_2 \sin^2\theta \cos\theta \cos 2\varphi,$$

$$Y_5 = \cos^5\theta - \frac{10}{9}\cos^3\theta + \frac{5}{21}\cos\theta$$

$$+ L_2 \sin^2\theta (\cos^3\theta - \frac{1}{3}\cos\theta) \cos 2\varphi$$

$$+ L_4 \sin^4\theta \cos\theta \cos 4\varphi \ \circ\circ\circ\circ\bullet$$

In the case where $\beta = \gamma$ symmetry further requires that

$$H_2 = 0, \quad L_2 = 0$$

One may now apply Green's theorem:

$$\int (U\frac{dV}{dn} - V\frac{dU}{dn}) \ ds = 0$$

to the surface of the region between the rectangle ABCD
and the sphere P. Within this region V satisfies
Laplace's equation, as also will U, if we take

$$U = x = r \cos\theta$$

The applied field is taken as parallel to AD, BC,
thus sides DC and AB are equipotential. Over the sides

BC, AD, $\frac{\partial J}{\partial n}$, $\frac{\partial V}{\partial n}$ both vanish. On CD, $\frac{\partial V}{\partial n}$ represents the field strength.

$$E = \frac{J}{(\sigma + j\omega K_0 \epsilon_0)} = \frac{J}{j\omega\epsilon_0 K_0^*}$$

where J is current density and

$$K_0^* = K_0^0 - j\frac{\sigma_0}{\omega\epsilon_0}$$

Therefore $\int \frac{dV}{dn}$ ds over CD, AB represents $\left[\frac{J\beta\gamma}{j\omega\epsilon_0 K_0^*}\right] \sigma$. The value of remainder of the integral

$-\int V\frac{du}{dn}$ ds, over the same lines is $-\beta\gamma V_1$ where V_1 is

the fall in potential corresponding to one rectangle, as between CD and AB.

On the spherical part of the contour over which Green's theorem is to be applied
$$U = a\cos\theta, \quad \frac{dU}{dn} = -\frac{dU}{dr} = -\cos\theta.$$

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$$V = A_0 + (A_1 a + B_1 a^{-2}) Y_1 + (A_3 a^3 + B_3 a^{-4}) Y_3 + \cdots$$

$$\frac{dV}{dn} = -\left.\frac{dV}{dr}\right|_{r=a} = -(A_1 - 2B_1 a^{-3}) Y_1 - (3A_3 a^2 - 4B_3 a^{-5}) Y_3 \cdots$$

Substituting these expressions into Green's theorem yields

$$\int (U\frac{dV}{dn} - V\frac{dU}{dn}) ds = \int U\frac{dV}{dn} ds - \int V\frac{dU}{dn} ds$$

$$= \int_0^{2\pi}\int_0^{\pi} (a \cos\theta) \left[-(A_1 - 2B_1 a^{-3})Y_1 - (3A_3 a^2 - 4B_3 a^{-5})Y_3 - \cdots\right]$$

$$\times (a^2 \sin\theta \, d\theta \, d\varphi) - \int_0^{2\pi}\int_0^{\pi} \left[A_0 + (A_1 a + B_1 a^{-2})Y_1 + (A_3 a^3 + B_3 a^{-4})Y_3 + \cdots\right]$$

$$\times (-\cos\theta)(a^2 \sin\theta \, d\theta \, d\varphi)$$

Inserting the appropriate expansions for Y_1, Y_3, $\cdots$ gives

$$\int (U\frac{dV}{dn} - V\frac{dU}{dn}) ds = -a^3(A_1 - 2B_1 a^{-3}) \int_0^{2\pi}\int_0^{\pi} (\cos\theta) \sin\theta \cos\theta \, d\theta \, d\varphi$$

$$-a^3(3A_3 a^2 - 4B_3 a^{-5}) \int_0^{2\pi}\int_0^{\pi} (\cos^3\theta - \frac{3}{5}\cos\theta + H_2\sin^2\theta\cos\theta\cos2\varphi)$$

$$\times \sin\theta \cos\theta \, d\theta \, d\varphi - \cdots + a^2 A_0 \int_0^{2\pi}\int_0^{\pi} \sin\theta \cos\theta \, d\theta \, d\varphi$$

$$+a^2(A_1 a + B_1 a^{-2}) \int_0^{2\pi}\int_0^{\pi} (\cos\theta) \sin\theta \cos\theta \, d\theta \, d\varphi$$

$$+a^2(A_3 a^3 + B_3 a^{-4}) \int_0^{2\pi}\int_0^{\pi} (\cos^3\theta - \frac{3}{5}\cos\theta + H_2\sin^2\theta \cos\theta \cos2\varphi)$$

$$\times \sin\theta \cos\theta \, d\theta \, d\varphi + \cdots$$

Simplifying,

$$\int (U\frac{dV}{dn} - V\frac{dU}{dn})ds = -(A_1 a^3 - 2B_1)I_1 - (3A_3 a^5 - 4B_3 a^{-2})(I_3 - \frac{3}{5}I_1 + H_2 I_2)$$

$$- \cdots + a^2 A_0 I_0 + (A_1 a^3 + B_1)I_1 + (A_3 a^5 + B_3 a^{-2})(I_3 - \frac{3}{5}I_1 + H_2 I_2) + \cdots$$

where

$$I_0 = \int_0^{2\pi} \int_0^{\pi} \sin\theta \cos\theta \; d\theta \; d\varphi = 0$$

$$I_1 = \int_0^{2\pi} \int_0^{\pi} (\cos\theta) \sin\theta \cos\theta \; d\theta \; d\varphi = \frac{2}{3}(2\pi) = \frac{4\pi}{3}$$

$$I_2 = \int_0^{2\pi} \int_0^{\pi} (\sin^2\theta \cos\theta \cos2\varphi) \sin\theta \cos\theta \; d\theta \; d\varphi = 0$$

$$I_3 = \int_0^{2\pi} \int_0^{\pi} (\cos^3\theta) \sin\theta \cos\theta \; d\theta \; d\varphi = \frac{2}{5}(2\pi) = \frac{4\pi}{5}$$

etc.

Thus

$$\int (U\frac{dV}{dn} = V\frac{dU}{dn})ds = -\frac{4\pi}{3}(A_1 a^3 - 2B_1) - (\frac{4\pi}{5} - \frac{3}{5} \cdot \frac{4\pi}{3})(3A_3 a^5 - 4B_3 a^{-2})$$

$$- \cdots + (A_1 a^3 + B_1)\frac{4\pi}{3} + (\frac{4\pi}{5} - \frac{3}{5} \cdot \frac{4\pi}{3})(3A_3 a^5 - 4B_3 a^{-2}) + \cdots$$

$$= 4\pi B_1$$

Although only terms up to Y_3 were used above, it is seen that integrals of the type $\int (\cos\theta)Y_n(\sin\theta \; d\theta \; d\varphi)$ will vanish for $n = 3, 5, 7, \cdots$ due to the particular numerical coefficients on powers of $\cos\theta$ in Y_n and also to terms which contain $\cos k\varphi$, $k = 2, 4, 6 \cdots$ since $\int_0^{2\pi} \cos k\varphi \; d\varphi = 0$, $k = 2, 4, 6 \cdots$.

Thus from Green's theorem one has finally,

$$\frac{J\beta\gamma\alpha}{j\omega\varepsilon_0 K_0^*} - \beta\gamma V_1 + 4\pi B_1 = 0$$

The potential V at any point may be regarded as due
to external sources at infinity (by which the flow is
caused) and to multiple sources situated on the axes of
the cylinders. The first part may be denoted by-Ex.
In considering the second it will conduce to clearness
if we imagine the (infinite) region occupied by the
cylinders to have a rectangular boundary parallel to
α and β. Even then the manner in which the infinite
system of sources is to be taken into account will depend
upon the shape of the rectangle. The simplest case,
which suffices for our purpose, is when we suppose the
rectangular boundary to be extended infinitely more
parallel to α than to β. It is then evident that the
periodic difference V_1 may be reckoned as due entirely
to-Ex, and equated to-Ec. For the difference due to the
sources upon the axes will be equivalent to the addition
of one extra column at $+ x$, and the removal of one at
$- \infty$, and in the case supposed such a transference is
immaterial.[*] Thus

$$V_1 = E\alpha$$

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[*] It would be otherwise if the infinite rectangle were
supposed to be of another shape, e.g. to be square.

Placing $V_1 = E\sigma$ in the above result obtained by use of Green's theorem, one obtains

$$\frac{J}{E} = [1 - \frac{4\pi B_1}{\alpha^3 \gamma E}] \ j\omega\varepsilon_0 K^*_0$$

E is the applied field so that $\frac{J}{E}$ is just the complex dielectric constant of the medium. For $\omega = 0$ it is just the specific conductivity in a direction parallel to α of the compound medium. It now remains to connect E with B_1.

Following Rayleigh we now calculate B_1/E approximately, limiting the treatment, for the sake of simplicity to the case of cubic order, that is where $\alpha = \beta = \gamma$.

One may now obtain a relationship between B_1 and E by equating two forms of the potential for a point x, y near P in appropriate limiting cases. For example, the potential at P due to multiple sources Q and source $-Ex$ at infinity is

$$V = \sum_{\xi, \eta, \zeta} \sum_n (A_n r'^n + B_n r'^{n-1}) Y'_n - Ex.$$

Here the r' and the arguments of the spherical harmonics are referred to coordinate system located at each Q. ξ, η, ζ denote the origin of the Q's. If the Q sources are allowed to recede to a great distance only the terms in B will contribute. The above expression does not include

the effect of P itself. On the other hand, if the
sphere P is excluded (if its radius goes to zero) the
potential at xy is given by our original expression
with the terms in B absent. Thus another form for the
potential is

$$A_o + A_1 r Y_1 + A_3 r^3 V_3 + \ldots$$

Equating the two forms, one has

$$A_o + A_1 x + A_3 \left(x^3 - \frac{3}{5} x r^2 \right) + \ldots \quad ,$$

$$= B_1 \Sigma \frac{x'}{r'^3} + B_3 \Sigma \frac{x'^3 - \frac{3}{5} x' r'^2}{r'^2} + \ldots$$

in which

$$x' = x - \xi, \quad y' = y - \eta, \quad z' = z - \zeta$$

where ξ, η, ζ are the coordinates of Q referred to P.
Hence by differentiating the left side once with respect
to x then setting $x = y = z = 0$, $A_1 - H$ is obtained and
is equated to the corresponding expression on the right
side. In similar fashion, differentiating the left side
thrice with respect to x then setting $x = y = z = 0$ yields
$3! A_3$, which is equated to the corresponding expression
on the right. Thus

$$A_1 - H = \left[\frac{d}{dx} \left\{ B_1 \Sigma \frac{x'}{r'^3} + B_3 \Sigma \frac{x'^3 - \frac{3}{5} x' r'^2}{r'^7} + \ldots \right\} \right]_{x=y=z=0}$$

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At the origin, $x = y = z = 0$ so that $\dfrac{d}{dx} \longrightarrow -\dfrac{d}{d\zeta}$ and

$$A_1 - H = B_2 \Sigma - \frac{d}{d\zeta}\left(\frac{x'}{r'^3}\right) + B_3 \Sigma - \frac{d}{d\zeta}\left(\frac{x'^3 - \frac{3}{5}x'r'^2}{r'^7}\right) + \cdots$$

Since $x' = -\zeta$, $y' = -\eta$, $z' = -\zeta$ at the origin, so
also is $r'^2 = \zeta^2 + \eta^2 + \zeta^2 = \rho^2$ and thus

$$-\frac{d}{d\zeta}\left(\frac{x'}{r'^3}\right) = -\frac{d}{d\zeta}\left(\frac{-\zeta}{\rho^3}\right) = \frac{\rho^3 = 3\rho^2\zeta\, d\rho/d\zeta}{\rho^6} = \frac{\rho^2 - 3\zeta^2}{\rho^5}$$

If we let $\mu = \zeta/\rho$, then

$$-\frac{d}{d\zeta}\left(\frac{x'}{r'^2}\right) = -\frac{2}{\rho^3}\,\frac{3\zeta^2 - \rho^2}{2\rho^2} = -\frac{2}{\rho^3}\left\{\frac{1}{2}(3\mu^2 - 1)\right\} = -\frac{2}{\rho^3}P_2(\mu)$$

where $P_2(\mu)$ is the second order Legendre polynomial. Also

$$-\frac{d}{d\zeta}\left(\frac{x'^3 - \frac{3}{5}x'r'^2}{r'^7}\right) = -\frac{d}{d\zeta}\left(\frac{-\zeta^3 + \frac{3}{5}\zeta\rho^2}{\rho^7}\right) =$$

$$= \frac{\rho^7[3\zeta^2 - \frac{3}{5}(\rho^2 + 2\zeta^2)] - 7\rho^5(\zeta^4 - \frac{3}{5}\zeta^2\rho^2)}{\rho^{14}}$$

$$= -\frac{1}{5\rho^5}\left[35\frac{\zeta^4}{\rho^4} - 30\frac{\zeta^2}{\rho^2} + 3\right] = -\frac{8}{5\rho^5}\left(\frac{35\mu^4 - 30\mu^2 + 3}{8}\right)$$

$$= -\frac{8P_4(\mu)}{5\rho^5}$$

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where $P_4(\mu)$ is the forth order Legendre polynomial.
Hence

$$A_1 - H = -2B_1 \Sigma \rho^{-3} P_2(\mu) - \frac{8}{5} B_3 \Sigma \rho^{-5} P_4(\mu) + \cdots$$

In similar fashion:

$$3! A_3 = \left[\frac{d^3}{dx^3} \left\{ B_1 \Sigma \frac{x'}{r'^3} + B_3 \Sigma \frac{x'^3 - \frac{3}{5} x' r'^2}{r'^7} + \cdots \right\} \right]_{x=y=z=0}$$

Again at the origin, $\dfrac{d^3}{dx^3} \longrightarrow - \dfrac{d^3}{d\zeta^3}$ so that

$$\frac{d^3}{dx^3} \left(\frac{x'}{r'^3} \right) = - \frac{d^3}{d\zeta^3} \left(\frac{-\zeta}{\rho^3} \right) = \frac{d^2}{d\zeta^2} \left(\frac{\rho^2 - 3\zeta^2}{\rho^5} \right) = \frac{d}{d\zeta} \left(\frac{15\zeta^3 - 9\zeta\rho^2}{\rho^7} \right)$$

$$= 15 \left[- \frac{d}{d\zeta} \left(\frac{-\zeta^3 + \frac{3}{5}\zeta\rho^2}{\rho^7} \right) \right] = 15 \left(- \frac{8 P_4(\mu)}{5\rho^5} \right) = -24 \frac{P_4(\mu)}{\rho^5}$$

while

$$\frac{d^3}{dx^3} \left(\frac{x'^3 - \frac{3}{5} x' r'^2}{r'^7} \right) = - \frac{d^3}{d\zeta^3} \left(\frac{-\zeta^3 + \frac{3}{5}\zeta\rho^2}{\rho^7} \right)$$

$$= \frac{d^2}{d\zeta^2} \left[6\zeta^2 \rho^{-7} - 7\zeta^4 \rho^{-9} + \frac{3}{5}\rho^{-5} \right]$$

$$= \frac{d}{d\zeta} \left[15\zeta\rho^{-7} - 70\zeta^3\rho^{-9} + 63\zeta^5\rho^{-11} \right]$$

$$= -3\rho^{-7} \left(231 \frac{\zeta^6}{\rho^6} - 315 \frac{\zeta^4}{\rho^4} + 105 \frac{\zeta^2}{\rho^2} - 5 \right)$$

$$= - \frac{48}{\rho^7} P_6(\mu)$$

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Hence

$$A_3 = -4B_1 \Sigma \rho^{-5} P_4(\mu) - 8B_3 \Sigma \rho^{-7} P_6(\mu) - \cdots$$

A similar procedure will give A_5, A_7, etc. Each of the above summations is over all the other spheres Q, i.e., over all coordinates ξ, η, ζ of the form $\ell\alpha$, $m\alpha$, $n\alpha$ where ℓ, m, n are positive and negative integers except 0, 0, 0. Let these sums be denoted by S_2, S_4, etc. so that

$$\Sigma \rho^{-n-1} P_n(\mu) = c^{-n-1} S_n$$

Since $A_n = B_n \left(\dfrac{1+\nu+1/n}{1-\nu} \right) \dfrac{1}{a^{2n+1}}$ due to the boundary conditions, we have the following:

$$A_3 = B_3 \frac{(1+\nu+1/3)}{(1-\nu) a^7} = -4B_1(c^{-5}S_4) - 8B_3(c^{-7}S_6) - \cdots$$

and thus

$$A_1 - H = B_1 \frac{(1+\nu+1)}{(1-\nu)a^3} - H = -2B_1(c^{-3}S_2) - \frac{8}{5} B_3(c^{-5}S_4) - \cdots$$

or

$$H = B_1 \left(\frac{2+\nu}{1-\nu} \right) \frac{1}{a^3} + 2B_1 c^{-3}S_2 + \frac{8}{5} c^{-5}S_4 \left[-4B_1 c^{-5}S_4 \cdot \frac{(1-\nu) a^7}{(\frac{4}{3} + \nu)} \right]$$

if we neglect the last term in the A_3 expansion.

Therefore

$$\frac{Ha^3}{B_1} = \frac{2+\nu}{1-\nu} + 2\left(\frac{a}{c}\right)^3 S_2 - \frac{32}{5}\left(\frac{a}{c}\right)^{10}\left(\frac{1-\nu}{\frac{4}{3}+\nu}\right)S_4^2 + \cdots$$

Finally, the specific conductivity is

$$1 - \frac{4\pi B_1}{c\beta\gamma H} = 1 - \frac{4\pi a^3}{c^3\left(\frac{Ha^3}{B_1}\right)} \quad \text{(where } c=\beta=\gamma \text{ for simplicity)}$$

$$= 1 - \frac{4\pi a^3/c^3}{\frac{2+\nu}{1-\nu} + 2\left(\frac{a}{c}\right)^3 S_2 - \frac{32}{5}\left(\frac{a}{c}\right)^{10}\left(\frac{1-\nu}{\frac{4}{3}+\nu}\right)S_4^2 + \cdots}$$

It remains to calculate the sums S_n. For the first sum S_2, we have

$$S_2 = \Sigma\, \rho^{-3} P_2(\mu) = \Sigma\, \frac{3\mu^2 - 1}{2\rho^3} = \Sigma\, \frac{2\xi^2 - \eta^2 - \zeta^2}{2\rho^5} = -\frac{1}{2}\Sigma\, \frac{d}{d\xi}\left(\frac{\xi}{\rho^3}\right)$$

It has been assumed that the extension of the medium is infinitely more parallel to the c direction than either β or γ so the space to be summed over is a rectangle bounded by $\xi = \pm\infty$, $\eta = \pm v$, $\zeta = \pm v$ where v will ultimately increase without limit.

Consider first the space bounded by $\xi = \eta = \zeta = \pm v$, a cube centered on the origin. Since the spheres Q are cubically symmetric, $\Sigma\, \frac{\xi^2}{\rho^5} = \Sigma\, \frac{\eta^2}{\rho^5} = \Sigma\, \frac{\zeta^2}{\rho^5}$ so that

$$S_2 = \Sigma\, \frac{2\xi^2 - \eta^2 - \zeta^2}{\rho^5} = 0 \quad \text{over this space.}$$

Consider next the space bounded by $\xi = \pm v$, $\zeta = \pm \infty$ $\eta = \zeta = \pm v$. We assume that in this space, ρ is sufficiently large so that the summation can be replaced by an integral. Hence

$$S_2 = -\frac{1}{2}\Sigma \frac{d}{d\xi}\left(\frac{\xi}{\rho^3}\right) = -\frac{1}{2}\int\int\int_{-v}^{v}\int_{-v}^{v} \frac{d}{d\xi}\left(\frac{\xi}{\rho^3}\right) d\xi\, d\eta\, d\zeta$$

where ξ is integrated from $-\infty$ to $-v$ and $+v$ to $+\infty$. Hence $\frac{1}{2}S_2$ will be obtained by integrating from $+v$ to $+\infty$.

$$S_2 = -\int_{v}^{\infty}\int_{-v}^{v}\int_{-v}^{v} \frac{d}{d\xi}\left(\frac{\xi}{\rho^3}\right) d\xi\, d\eta\, d\zeta = \int_{-v}^{v}\int_{-v}^{v}\left[\frac{\xi}{\rho^3}\right]_{v}^{\infty} d\eta\, d\zeta$$

$$= -\int_{-v}^{v}\int_{-v}^{v}\frac{-v\, d\eta\, d\zeta}{(v^2+\eta^2+\zeta^2)^{3/2}} = +v\int_{-v}^{v}\left[\frac{\eta}{(v^2+\zeta^2)(v^2+\eta^2+\zeta^2)^{1/2}}\right]_{-v}^{v} d\zeta$$

$$= 2v^2\int_{-v}^{v}\frac{d\zeta}{(v^2+\zeta^2)(2v^2+\zeta^2)^{1/2}}$$

Let $\zeta = v\tan\theta$, then $d\zeta = v\sec^2\theta\, d\theta$, $v^2+\zeta^2 = v^2\sec^2\theta$,

$(2v^2+\zeta^2)^{1/2} = v(2+\tan^2\theta)^{1/2}$, $\zeta = v \longrightarrow \theta = \frac{\pi}{4}$

$\zeta = -v \longrightarrow \theta = -\frac{\pi}{4}$ so that the above integral becomes

$$S_2 = \int_{-\pi/4}^{\pi/4}\frac{2d\theta}{\sqrt{2+\tan^2\theta}}$$

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Let $x = \sin\theta$, then $dx = \cos\theta\, d\theta$, $\tan^2\theta = \dfrac{x^2}{1-x^2}$,

$\theta = \dfrac{\pi}{4} \longrightarrow x = \dfrac{1}{\sqrt{2}}$, $\theta = -\dfrac{\pi}{4} \longrightarrow x = -\dfrac{1}{\sqrt{2}}$ and we have

$$S_2 = 2 \int_{-1/\sqrt{2}}^{1/\sqrt{2}} \frac{dx}{\sqrt{2-x^2}} = 2\left[\sin^{-1}\left(\frac{x}{\sqrt{2}}\right)\right]_{-1/\sqrt{2}}^{1/\sqrt{2}} = \frac{2\pi}{3}$$

Finally if we let $p = \dfrac{4\pi a^3}{3\,\alpha^3}$ and neglect the term containing $\left(\dfrac{a}{\alpha}\right)^{10}$ as a first approximation to the specific conductivity, we obtain

$$1 - \frac{4\pi B_1}{\alpha^3 H} = 1 - \frac{3p}{\dfrac{2+\nu}{1-\nu} + 2\left(\dfrac{3p}{4\pi}\right)\left(\dfrac{2\pi}{3}\right)} = \frac{\dfrac{2+\nu}{1-\nu} - 2p}{\dfrac{2+\nu}{1-\nu} + p}$$

In order to carry on the approximation we must calculate S_4, etc. An approximate value of S_4 may be calculated by direct summation from the formula

$$S_4 = \Sigma \frac{35\xi^4 - 30\xi^2\rho^2 + 3\rho^4}{8\rho^2}$$

We may limit ourselves to the consideration of positive and zero values of ξ, η, ζ . Every term for which ξ, η, ζ are finite is repeated in each octant, that is 8 times. If one of the three coordinates vanish, the repetition is fourfold, and if two vanish, twofold.

The following table contains the result for all
points which lie within $\rho^2 = 18$. This repetition in the
case, for example, of $\rho^2 = 9$ represents two kinds of
composition. In the first

$$\rho^2 = 2^2 + 2^2 + 1^2 = 9,$$

and in the second

$$\rho^2 = 3^2 + 0^2 + 0 = 9.$$

The success of the approximation is favored by the fact
that P vanishes when integrated over the complete
sphere, so that the sum required is only a kind of
residue depending upon the discontinuity of the
summation.

The result is

$$S_4 = 3.11 \circ\circ\circ\circ\circ\circ\circ\circ\circ\circ\circ$$

	ρ^2			ρ^2	
0,0,1	1	+3.5000	0,0,3	9	+.0144
0,1,1	2	- .3094	0,1,3	10	+.0243
1,1,1	3	- .1996	1,1,3	11	+.0075
0,0,2	4	+ .1094	2,2,2	12	-.0062
0,1,2	5	+ .0501	0,2,3	13	-.0015
1,1,2	6	- .0397	1,2,3	14	-.0095
0,2,2	8	- .0097	0,0,4	16	+.0034
1,2,2	9	- .0277	2,2,3	17	-.0061
			0,1,4	17	+.0085

As indicated earlier the preceding several pages for evaluating E/B_1 follow Rayleigh. Details have been added.

Referring to our formula for complex dielectric constant (taking $\alpha = \beta = \gamma$)

$$K_e^* = [1 - \frac{4\pi}{a^3 \, E/B_1}] \, K_0^*$$

One may now insert in the above the following expression for E/B_1

$$\frac{E}{B_1} = \frac{1}{a^3} \left[- \frac{1+2\epsilon_0^*/\epsilon_s^*}{1-\epsilon_0^*/\epsilon_s^*} + \frac{4\pi}{3} \frac{a^3}{a^3} - \frac{32}{5} \frac{(1-\epsilon_0^*/\epsilon_s^*)(3.11)^2}{2\epsilon_0^*/\epsilon_s^*+1-2\epsilon_0^*/3\epsilon_s^*} \frac{a^{10}}{a^{10}} + \, _{o\,o} \right]$$

We now wish to compare the above expression for K_e^* with our form for K_e^*, that is with the Lorentz method for obtaining K_e^*. In the latter case we have (in c g s) units

$$K_e^* = 1 + \frac{4\pi n_0 \alpha'}{1-4\pi n_0 \alpha'/3} = \frac{1+4\pi n_0 \alpha' \, 2/3}{1-4\pi n_0 \alpha'/3}$$

In this case α' is the polarizability of an impurity sphere.

First note that if $4\pi n_0 \alpha'/3$ is much less than unity one can write the above

$$K_e^* \cong 1 + 4\pi n_0 \alpha'$$

Also note that this is the form one would obtain
for K_e^* if it is assumed that the local field is equal
to the external field.[*] That is, it is the form of K_e^*
when one neglects the effect of the spheres on each
other.

$$\sigma' = \frac{1 - \varepsilon_0^*/\varepsilon_s^*}{1 + 2\varepsilon_0'^*/\varepsilon_s^*} \; a^3$$

Putting this in our approximate expression for K_e^*, one
has

$$K_e^* \leq 1 + 4\pi n_0 a^3 \left(\frac{1 - \varepsilon_0^*/\varepsilon_s^*}{1 + 2\varepsilon_0'^*/\varepsilon_s^*} \right)$$

If one approximates E/B_1 by

$$\frac{E}{B_1} = - \frac{1}{a^3} \left[\frac{2\varepsilon_0^*/\varepsilon_s^* + 1}{\varepsilon_0^*/\varepsilon_s - 1} \right]$$

---

[*]
$$P = \chi E$$

Also $P = n_0 \sigma' E_{eff} = n_0 \sigma' E$

if local field E_{eff} is equal to applied field E.

Therefore
$$\chi = n_0 \sigma'$$

and
$$K = 1 + 4\pi\chi = 1 + 4\pi n_0 \sigma'$$

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In the Rayleigh general result

$$K_e^* = [1 - \frac{4\pi}{\sigma^3 E/B_1}]K_0^*$$

one has

$$K_e^* = 1 + \frac{4\pi a^3}{\sigma^3}\left[\frac{1 - \epsilon_0^*/\epsilon_s^*}{1 + 2\epsilon_0^*/\epsilon_s^*}\right]$$

$\frac{1}{\sigma^3} = n_0 =$ number of spheres per unit volume. Thus

employing the first term only in the Rayleigh expansion
is equivalent to the Lorentz treatment when the local
electric field is equal to tho external applied field.
Since this is not true in our case, the Rayleigh result
using only the first term in the E/B_1 expansion results
in a poor approximation.

Now examine the effect of including the second term
in E/B_1. The first term is simply the reciprocal of the
polarizability, σ', of a single impurity sphere. Thus

$$E/B_1 = [-\frac{1}{\sigma'} + \frac{4\pi n_0}{3}]$$

Putting this in the Rayleigh expression for K_e^*

$$K_e^* = 1 - \frac{4\pi n_0}{-\frac{1}{\sigma'} + \frac{4\pi n_0}{3}} = 1 + \frac{4\pi n_0 \sigma'}{1 - \frac{4\pi n_0 \sigma'}{3}}$$

This is our general result using the Lorentz procedure.
Thus one can say that the inclusion of the first two
terms in the expansion for E/B_1 in the Rayleigh method
is equivalent to the Lorentz procedure. The third term
in Rayleigh's procedure will represent the improvement
to be gained from the more exact procedure. In view
of the above results, it is now convenient to write
E/B_1 as follows

$$E/B_1 = \left[-\frac{1}{\sigma'} + \frac{4\pi n_0}{3} - \frac{32}{5} \frac{\sigma' a^4 (3.11)^2}{n_0^{10/3} \left[1 - \frac{2\epsilon_0^*/\epsilon_s^*}{3(1+2\epsilon_0^*/\epsilon_s^*)} \right]} \right]$$

$$= \left[-\frac{1}{\sigma'} + \frac{4\pi n_0}{3} - \frac{4\pi n_0 c}{3} \right]$$

$\frac{4\pi n_0 c}{3}$ stands for the third order correction terms.

Then the Rayleigh K_e^* may be written

$$K_e^* = 1 - \frac{4\pi n_0}{-\frac{1}{\sigma'} + \frac{4\pi n_0}{3}(1 - c)} = 1 + \frac{4\pi n_0 \sigma'}{1 - \frac{4\pi n_0}{3}(1 - c)\sigma'}$$

Thus the Rayleigh treatment is equivalent to writing for
the effective field (in cgs)

$$E_{eff} = E_0 + \Upsilon P$$

where
$$\gamma = \frac{4\pi(1-c)}{3}$$

rather than simply $\gamma = \frac{4\pi}{3}$.

Since there is no advantage in displaying the polarizability α' in c, we write c as follows for computational purposes.

$$c = \frac{32}{5}(3.11)^{2} \; \frac{1 - \epsilon_{0}^{*}/\epsilon_{s}^{*}}{(1+4\epsilon_{0}^{*}/3\epsilon_{s}^{*})} \; \frac{a^{10}}{\alpha^{10}} \; \frac{1}{n_{0}a^{3}}$$

$$\frac{a^{10}}{\alpha^{10}} = \left(\frac{a^{3}}{\alpha^{3}}\right)^{10/3} = (n_{0}a^{3})^{10/3} = B^{10/3}$$

where $B = n_{0}a^{3} = \frac{3n_{0}v}{4\pi}$. v is the volume of a single impurity sphere and n_{0}, as before, the number of such spheres per unit volume.

$$c = 6.190\left[\frac{1-\epsilon_{0}^{*}/\epsilon_{s}^{*}}{1+4\epsilon_{0}^{*}/3\epsilon_{s}^{*}}\right] B^{7/3} = 2.188 \left[\frac{1-\epsilon_{0}^{*}/\epsilon_{s}^{*}}{1+4\epsilon_{0}^{*}/3\epsilon_{s}^{*}}\right](n_{0}v)^{7/3}$$

From this result it is clear that the accuracy of the Lorentz-type treatment depends not only on the fractional volume occupied by impurity spheres but it also depends

on the ratio of the medium to impurity dielectric
properties as was to be expected.

We examine c for the limiting cases of a pure
dielectric impurity ($\sigma = 0$) and for a pure conducting
impurity.

Dielectric case

$$c = 61.90 \left[\frac{1-K_o/K_s}{1+4K_o/3K_s} \right] B^{7/3} = 2.188 \left[\frac{1-K_o/K_s}{1+4K_o/3K_s} \right] (n_o v)^{7/3}$$

Conducting spheres

$$c = 61.90 \left[\frac{1-\sigma_o/\sigma_s}{1+4\sigma_o/3\sigma_s} \right] B^{7/3} = 2.188 \left[\frac{1-\sigma_o/\sigma_s}{1+4\sigma_o/\sigma_s} \right] (n_o v)^{7/3}$$

Intermediate cases must be examined by equating
real and imaginary parts of our general expression for
K_e^*. Results will also be frequency dependent.
Expressions for K_e and σ_e must then be compared with
those obtained from the Lorentz-type treatment.

We shall use the criterion that c must be less
than 0.1. Figures 3 and 4 show K_o/K_s as a function of
the fractional volume $n_o v$ for $c = -0.1$ and $c = +0.1$
respectively. Note that a large variation of K_o/K_s
(2 to greater than 10) is permitted when the impurity
content is as great as 2/5 of the volume of the sample.
Similarly, when K_o/K_s is less than 0.4, fractional volume
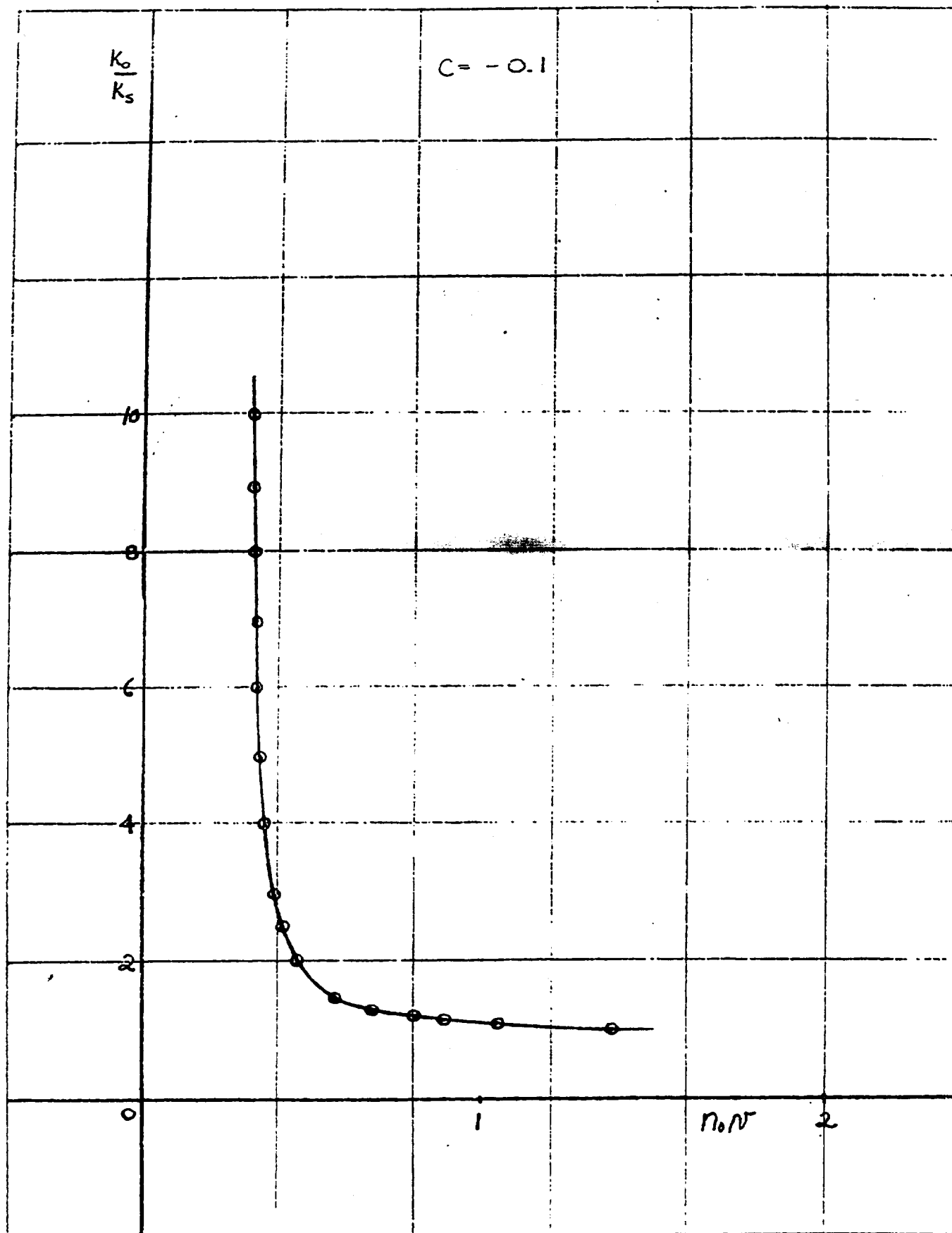
Figure 3. K_o/K_s as a function of fractional volume $n_o v$ for c = -0.1.

Figure 4. K_0/K_s as a function of fractional volume $n_0 v$ for $c = +0.1$.

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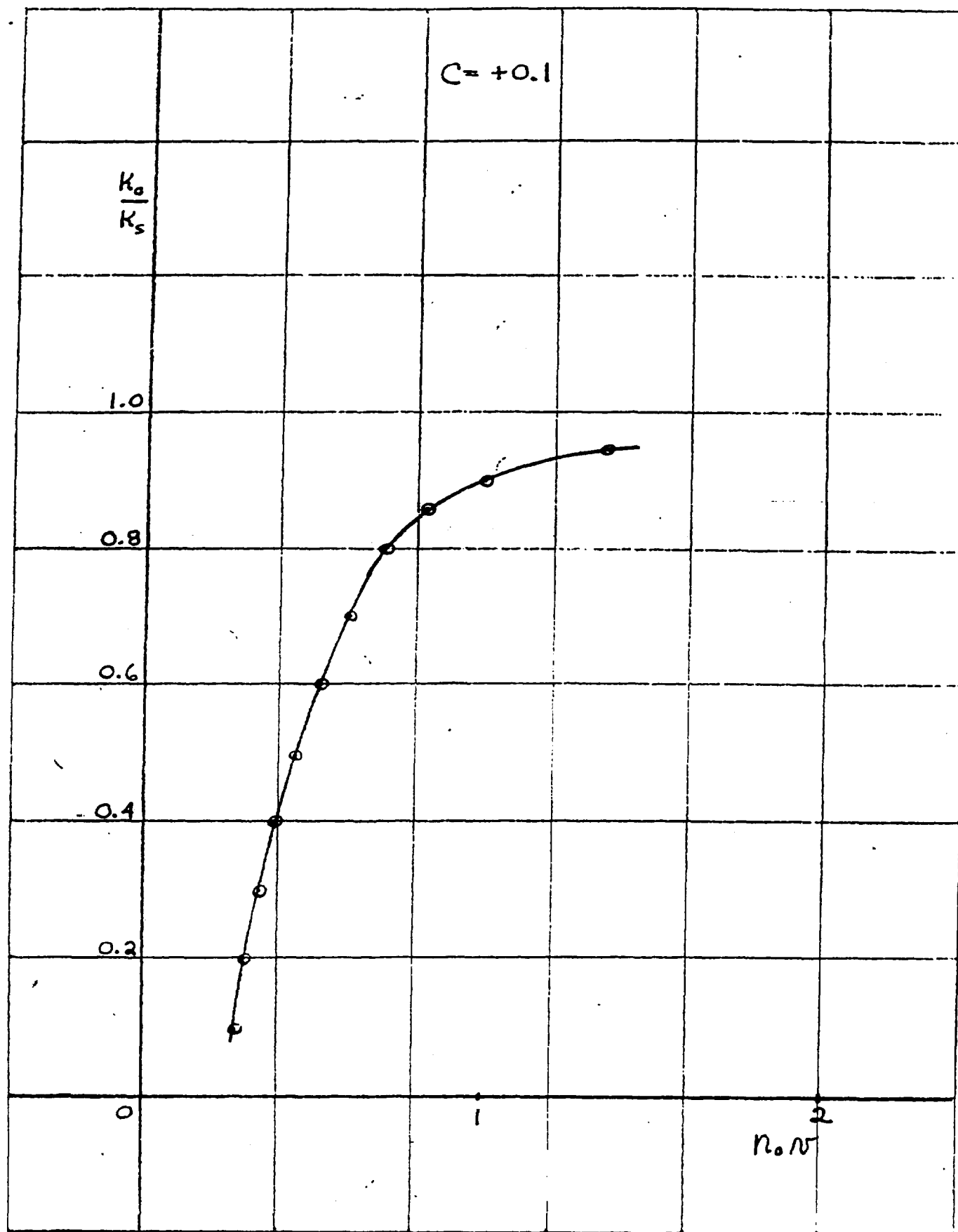
of the allowable impurity may range as high as 20 to 40 percent for the Lorentz model to remain valid. Thus one can conclude that for reasonable ratios of the dielectric properties of the sustaining medium to the impurity medium, the Lorentz model may be applied with considerable accuracy even though the fractional volume of impurity becomes rather large, that is, of the order of 20 to 40 percent.

Conclusions and Recommendations

The dielectric properties of a medium are sensitive in the microwave region to the impurity content. If time and interest permits, it would be worthwhile to develop the type of model described in this chapter so as to include radiative effects which will occur at the very high frequencies. In the event that further determinations are made of the dielectric constant and loss tangent of lead azide in the microwave region, one should look for the characteristic behavior displayed by the curves in this chapter in order to determine whether impurity effects may be significant.

Chapter V
CALCULATION OF THE DIELECTRIC PROPERTIES OF A
MEDIUM WHICH CONTAINS SPHERICAL DIELECTRIC PARTICLES
D. E. Schwalm

Consider a uniform dielectric medium, hereafter designated
as the support medium and denoted by a subscript $_o$, which
contains a cubical or random array of imbedded spherical particles,
hereafter designated as the impurity medium and denoted by the
subscript $_s$. The support medium will be characterized by a
dielectric constant K_o and a conductivity σ_o while the impurity
medium will be characterized by a dielectric constant K_s and a
conductivity σ_s. It is desired to obtain the resultant behavior
of the combined media which can be characterized by some "effective"
dielectric constant K_e and some "effective" conductivity σ_e .

In a paper on the THEORY OF THE DIELECTRIC CONSTANT, D. G.
Burkhard has derived an extended version of the usual Clausius-
Mosotti equation. We summarize that derivation here. Three
basic equations of electromagnetic theory lead to the Clausius-
Mosotti result. They are

$$P = \epsilon_o'^* \chi_e^* E_o$$

$$P = n_o \epsilon_o'^* \alpha E_{eff}$$

$$E_{eff} = E_o + \frac{P}{3\epsilon_o'^*}$$

where $\epsilon_o'^* = \epsilon_o K_o^*$ is the complex permittivity of the support
medium, χ_e^* is the effective complex susceptibility, α is
the polarizability of a spherical impurity, and E_{eff} is the local
field in the vicinity of an impurity sphere. The E_{eff} is
obtained by calculating the field in a spherical cavity due to the
polarization of the support medium and the field due to other
impurity spheres in the cavity. Since it is assumed that the

impurity spheres form either a cubic or random array, this latter field vanishes.

Elimination of P, E_o, and E_{eff} yields

$$\chi_e^* = \frac{n_o \alpha}{1 - \frac{1}{3} n_o \alpha}$$

However, to complete the derivation we need to use the conventional relations that exist between the ordinary dielectric constant and conductivity and the complex dielectric constant, namely

$$\chi_e^* = K_c^* - 1$$

$$K_c^* = \epsilon_e^* / \epsilon_o'^*$$

$$K^* = \left(K' - j \frac{\sigma}{\omega \epsilon_o} \right) = K' - j K''$$

$$\epsilon^* = \epsilon_o K^* = \left(\epsilon_o K' - j \frac{\sigma}{\omega} \right) = \left(\epsilon' - j \frac{\sigma}{\omega} \right)$$

Thus we obtain

$$\epsilon_e^* = \epsilon_o'^* \left[1 + \frac{n_o \alpha}{1 - n_o \alpha / 3} \right]$$

$$\epsilon_e' - j \frac{\sigma_e}{\omega} = \left(\epsilon_o' - j \frac{\sigma_o}{\omega} \right) \frac{1 + \frac{2}{3} n_o \alpha}{1 - \frac{1}{3} n_o \alpha}$$

$$\frac{\sigma_e}{\epsilon_o} + j \omega K_e = \left(\frac{\sigma_o}{\epsilon_o} + j \omega K_o \right) \left[\frac{1 + \frac{2}{3} n_o \alpha}{1 - \frac{1}{3} n_o \alpha} \right]$$

Now it remains to calculate the α of one of the imbedded spheres to complete the derivation.

Assume that the volume loading is small so that the problem of finding α reduces approximately to the problem of determining α for a single dielectric sphere in an infinite medium. In this case, solution of Laplace's equation yields for

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the potential outside the sphere

$$\varphi = \left(\frac{\epsilon_s^* - \epsilon_o'^*}{2\epsilon_o'^* + \epsilon_s^*} \, \frac{a^3}{r^3} - 1 \right) E_{eff} \, z$$

which consists of a dipole term and a uniform field term. The dipole potential is

$$\varphi_{dipole} = \frac{p z}{r^3} = \frac{p \cos\theta}{r^2}$$

so that the dipole moment is thus

$$P = \frac{\epsilon_s^* - \epsilon_o'^*}{2\epsilon_o'^* + \epsilon_s^*} \, a^3 E_{eff}$$

and so

$$\alpha = \frac{\epsilon_s^* - \epsilon_o'^*}{2\epsilon_o'^* + \epsilon_s^*} \, a^3 = \frac{1 - \epsilon_o'^* / \epsilon_s^*}{1 + 2 \, \epsilon_o'^* / \epsilon_s^*}$$

where a is the radius of an impurity sphere. Substituting this value of α into the Clausius-Mosotti equation yields

$$\frac{\sigma_e}{\epsilon_o} + j\omega K_e = \left(\frac{\sigma_o}{\epsilon_o} + j\omega K_o \right) \frac{1 + \frac{2}{3} n_o a^3 \left[1 - \dfrac{-\frac{j\epsilon_o}{\omega}\left(\frac{\sigma_o}{\epsilon_o} + j\omega K_o\right)}{-\frac{j\epsilon_o}{\omega}\left(\frac{\sigma_s}{\epsilon_o} + j\omega K_s\right)} \Big/ \left(1 + 2 \dfrac{-\frac{j\epsilon_o}{\omega}\left(\frac{\sigma_o}{\epsilon_o} + j\omega K_o\right)}{-\frac{j\epsilon_o}{\omega}\left(\frac{\sigma_s}{\epsilon_o} + j\omega K_s\right)} \right) \right]}{1 - \frac{1}{3} n_o a^3 \left[1 - \dfrac{-\frac{j\epsilon_o}{\omega}\left(\frac{\sigma_o}{\epsilon_o} + j\omega K_o\right)}{-\frac{j\epsilon_o}{\omega}\left(\frac{\sigma_s}{\epsilon_o} + j\omega K_s\right)} \Big/ \left(1 + 2 \dfrac{-\frac{j\epsilon_o}{\omega}\left(\frac{\sigma_o}{\epsilon_o} + j\omega K_o\right)}{-\frac{j\epsilon_o}{\omega}\left(\frac{\sigma_s}{\epsilon_o} + j\omega K_s\right)} \right) \right]}$$

where expressions for $\epsilon_o'^*$ and ϵ_s^*, namely

$$\epsilon_o'^* = -\frac{j\epsilon_o}{\omega}\left(\frac{\sigma_o}{\epsilon_o} + j\omega K_o \right) \quad \text{and} \quad \epsilon_s^* = -\frac{j\epsilon_o}{\omega}\left(\frac{\sigma_s}{\epsilon_o} + j\omega K_s \right)$$

have been substituted.

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This expression can now be reduced to obtain explicit equations for σ_e and K_e which is the final desired result. If we write

$$B = n_o a^3$$

$$\sigma = \frac{1}{\epsilon_o}\left(\sigma_s + 2\sigma_o\right) \quad ; \quad K = K_s + 2K_o$$

$$\sigma' = \frac{1}{\epsilon_o}\left(\sigma_s - \sigma_o\right) \quad ; \quad K' = K_s - K_o$$

then

$$\alpha = \frac{\left(\frac{\sigma_s}{\epsilon_o} + j\omega K_s\right) - \left(\frac{\sigma_o}{\epsilon_o} + j\omega K_o\right)}{\left(\frac{\sigma_s}{\epsilon_o} + j\omega K_s\right) + 2\left(\frac{\sigma_o}{\epsilon_o} + j\omega K_o\right)} a^3 = \frac{\frac{1}{\epsilon_o}\left(\sigma_s - \sigma_o\right) + j\omega\left(K_s - K_o\right)}{\frac{1}{\epsilon_o}\left(\sigma_s + 2\sigma_o\right) + j\omega\left(K_s + 2K_o\right)} a^3$$

$$= \frac{\sigma' + j\omega K'}{\sigma + j\omega K} a^3$$

so that the Clausius-Mosotti equation becomes

$$\frac{\sigma_e}{\epsilon_o} + j\omega K_e = \left(\frac{\sigma_o}{\epsilon_o} + j\omega K_o\right) \frac{1 + \frac{2}{3} n_o a^3 \left(\frac{\sigma' + j\omega K'}{\sigma + j\omega K}\right)}{1 - \frac{1}{3} n_o a^3 \left(\frac{\sigma' + j\omega K'}{\sigma + j\omega K}\right)}$$

$$= \left(\frac{\sigma_o}{\epsilon_o} + j\omega K_o\right) \frac{1 + \frac{2}{3} B \left(\frac{\sigma' + j\omega K'}{\sigma + j\omega K}\right)}{1 - \frac{1}{3} B \left(\frac{\sigma' + j\omega K'}{\sigma + j\omega K}\right)}$$

$$= \frac{\sigma_o}{\epsilon_o} \frac{\left(\sigma + \frac{2}{3}B\sigma'\right) + j\omega\left(K + \frac{2}{3}BK'\right)}{\left(\sigma - \frac{1}{3}B\sigma'\right) + j\omega\left(K - \frac{1}{3}BK'\right)} + j\omega K_o \frac{\left(\sigma + \frac{2}{3}B\sigma'\right) + j\omega\left(K + \frac{2}{3}BK'\right)}{\left(\sigma - \frac{1}{3}B\sigma'\right) + j\omega\left(K - \frac{1}{3}BK'\right)}$$

If subscript α denotes the form $X + \frac{2}{3}Bx'$ and subscript β denotes the form $X - \frac{1}{3}Bx'$, then

$$\frac{\sigma_e}{\epsilon_o} + j\omega K_e = \frac{\sigma_o}{\epsilon_o}\left(\frac{\sigma_\alpha + j\omega K_\alpha}{\sigma_\beta + j\omega K_\beta}\right) + j\omega K_o\left(\frac{\sigma_\alpha + j\omega K_\alpha}{\sigma_\beta + j\omega K_\beta}\right)$$

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$$\frac{\sigma_e}{\epsilon_o} + j\omega k_e = \frac{\left(\frac{\sigma_o}{\epsilon_o} + j\omega K_o\right)\left(\sigma_\alpha + j\omega K_\alpha\right)}{\left(\sigma_\beta + j\omega K_\beta\right)} \cdot \frac{\sigma_\beta - j\omega K_\beta}{\sigma_\beta - j\omega K_\beta}$$

$$= \frac{\frac{\sigma_o}{\epsilon_o}\left(\sigma_\alpha\sigma_\beta + \omega^2 K_\alpha K_\beta\right) - \omega^2 K_o\left(\sigma_\beta K_\alpha - \sigma_\alpha K_\beta\right) + j\omega\left[\frac{\sigma_o}{\epsilon_o}\left(\sigma_\beta K_\alpha - \sigma_\alpha K_\beta\right) + K_o\left(\sigma_\alpha\sigma_\beta + \omega^2 K_\alpha K_\beta\right)\right]}{\sigma_\beta^2 + \omega^2 K_\beta^2}$$

Separating and equating real and imaginary parts gives

$$\frac{\sigma_e}{\epsilon_o} = \frac{\frac{\sigma_o}{\epsilon_o}\left(\sigma_\alpha\sigma_\beta + \omega^2 K_\alpha K_\beta\right) - \omega^2 K_o\left(\sigma_\beta K_\alpha - \sigma_\alpha K_\beta\right)}{\sigma_\beta^2 + \omega^2 K_\beta^2}$$

and

$$K_e = \frac{\frac{\sigma_o}{\epsilon_o}\left(\sigma_\beta K_\alpha - \sigma_\alpha K_\beta\right) + K_o\left(\sigma_\alpha\sigma_\beta + \omega^2 K_\alpha K_\beta\right)}{\sigma_\beta^2 + \omega^2 K_\beta^2}$$

Replacing σ_α by $\sigma + \frac{2}{3}B\sigma'$, σ_β by $\sigma - \frac{1}{3}B\sigma'$, K_α by $K + \frac{2}{3}BK'$, K_β by $K - \frac{1}{3}BK'$ and separating out the ω dependent terms we obtain as intermediate results

$$\frac{K_e}{K_o} = \frac{\left(\sigma + \frac{2}{3}B\sigma'\right)\left(\sigma - \frac{1}{3}B\sigma'\right) + \frac{B\sigma_o}{K_o\epsilon_o}\left(\sigma K' - \sigma' K\right) + \omega^2\left(K + \frac{2}{3}BK'\right)\left(K - \frac{1}{3}BK'\right)}{\left(\sigma - \frac{1}{3}B\sigma'\right)^2 + \omega^2\left(K - \frac{1}{3}BK'\right)^2}$$

and

$$\frac{\sigma_e}{\sigma_o} = \frac{\left(\sigma + \frac{2}{3}B\sigma'\right)\left(\sigma - \frac{1}{3}B\sigma'\right) - \frac{BK_o\epsilon_o}{\sigma_o}\omega^2\left(\sigma K' - \sigma' K\right) + \omega^2\left(K + \frac{2}{3}BK'\right)\left(K - \frac{1}{3}BK'\right)}{\left(\sigma - \frac{1}{3}B\sigma'\right)^2 + \omega^2\left(K - \frac{1}{3}BK'\right)^2}$$

Now

$$\sigma + \frac{2}{3}B\sigma' = \frac{1}{\epsilon_o}\left[\left(1 + \frac{2}{3}B\right)\sigma_s + \left(2 - \frac{2}{3}B\right)\sigma_o\right]$$

$$\sigma - \frac{1}{3}B\sigma' = \frac{1}{\epsilon_o}\left[\left(1 - \frac{1}{3}B\right)\sigma_s + \left(2 + \frac{1}{3}B\right)\sigma_o\right]$$

$$\sigma K' - \sigma' K = \frac{3}{\epsilon_o}\left[\sigma_o K_s - \sigma_s K_o\right]$$

However, $B = n_o a^3 = \frac{4\pi a^3}{3}\left(\frac{3n_o}{4\pi}\right) = \frac{3}{4\pi} n_o v$

$$= \frac{3}{4\pi}(\text{ fractional volume occupied by impurities })$$

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To be consistent with the model, the fractional volume of impurities must certainly not exceed 25%. Even then, $B \simeq 0.06$ so that the error introduced into $\sigma + \frac{2}{3} B\sigma'$, $\sigma - \frac{1}{3} B\sigma'$, $K + \frac{2}{3} BK'$, and $K - \frac{1}{3} BK'$ by neglecting B relative to unity will not exceed $\sim 4\%$. For plotting purposes, this error is negligible. Thus we write

$$\frac{K_e}{K_o} = \frac{\sigma^2 + \omega^2 K^2 + \frac{B\sigma_o}{\epsilon_o K_o}\left(\sigma K' - K\sigma'\right)}{\sigma^2 + \omega^2 K^2}$$

$$\frac{\sigma_e}{\sigma_o} = \frac{\sigma^2 + \omega^2 K^2 - \frac{B K_o \epsilon_o}{\sigma_o}\left(\sigma K' - K\sigma'\right)\omega^2}{\sigma^2 + \omega^2 K^2}$$

or

$$\frac{K_e}{K_o} = 1 + \epsilon_o^2 \frac{B\sigma_o}{\epsilon_o K_o}\left[\frac{\frac{3}{\epsilon_o}\left(\sigma_o K_s - \sigma_s K_o\right)}{\left(\sigma_s^2 + 4\sigma_s \sigma_o + 4\sigma_o^2\right) + \epsilon_o^2 \omega^2\left(K_s^2 + 4K_s K_o + 4K_o^2\right)}\right]$$

$$\frac{\sigma_e}{\sigma_o} = 1 + \epsilon_o^2 \frac{B K_o \epsilon_o}{\sigma_o}\left[\frac{\frac{3}{\epsilon_o}\left(\sigma_s K_o - \sigma_s K_o\right)\omega^2}{\left(\sigma_s^2 + 4\sigma_s \sigma_o + 4\sigma_o^2\right) + \epsilon_o^2 \omega^2\left(K_s^2 + 4K_s K_o + 4K_o^2\right)}\right]$$

Now introduce the following ratios:

$$\phi = \frac{\sigma_s}{\sigma_o} \quad ; \quad \theta = \frac{K_s}{K_o} \quad ; \quad \rho = \frac{K_o}{\sigma_o}$$

Then

$$\frac{K_e}{K_o} = 1 + \frac{3B(\theta - \phi)}{(\phi^2 + 4\phi + 4) + \epsilon_o^2 \rho^2 \omega^2(\theta^2 + 4\theta + 4)}$$

$$\frac{\sigma_e}{\sigma_o} = 1 + \frac{3B(\phi - \theta)\epsilon_o^2 \rho^2 \omega^2}{(\phi^2 + 4\phi + 4) + \epsilon_o^2 \rho^2 \omega^2(\theta^2 + 4\theta + 4)}$$

As $3B\phi \ll 4\phi$ and $3B\theta \ll 4\theta$ to the same approximation previously made, i.e. neglect of B compared to unity, the above two expressions will reduce to

$$\frac{K_e}{K_o} = 1 + \frac{3B\theta}{(\phi^2 + 4\phi + 4) + \epsilon_o^2 \rho^2 \omega^2(\theta^2 + 4\theta + 4)}$$

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and
$$\frac{\sigma_e}{\sigma_0} = 1 + \frac{3B\phi\left(\epsilon_0^2\rho^2\omega^2\right)}{\left(\phi^2+4\phi+4\right)+\epsilon_0^2\rho^2\omega^2\left(\theta^2+4\theta+4\right)}$$

This is the form which will be most convenient for plotting. In the accompanying graphs, K_e/K_0 and σ_e/σ_0 have been plotted for the selected values of θ = 10, 100, 1000, and 10,000 and ϕ = 10, 10^3, 10^5, 10^7, and 10^9 over a range of ω from ω = 1 to ω = 10^{18}/sec. The value of ρ has been taken to be $\rho = K_0/\sigma_0 = 5 \times 10^{-18}$ sec^2.

It can be seen that $\frac{K_e}{K_0} \rightarrow 1$ as $\omega \rightarrow \infty$, $\frac{\sigma_e}{\sigma_0} \rightarrow 1$ as $\omega \rightarrow 0$, $\frac{K_e}{K_0} \rightarrow 1 + \frac{3B\theta}{\phi^2+4\phi+4}$ as $\omega \rightarrow 0$, and $\frac{\sigma_e}{\sigma_0} \rightarrow 1 + \frac{3B\phi}{\phi^2+4\phi+4}$ as $\omega \rightarrow \infty$. Thus the general shape of all curves will be
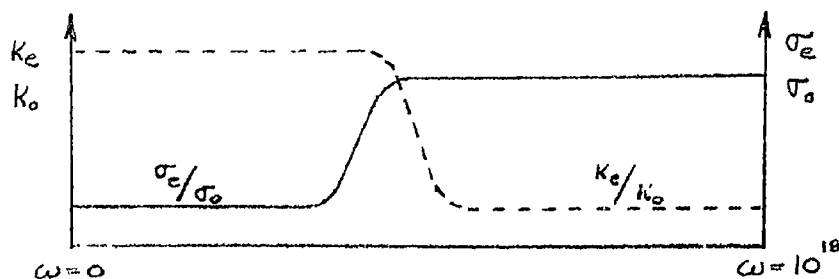
If we return to the intermediate results, we can evaluate the limits of K_e/K_0 and σ_e/σ_0 as $K_s \rightarrow \infty$ which corresponds to metallic impurities. Thus

$$\lim_{\substack{K_s \to \infty \\ \omega \to \infty}} \frac{K_e}{K_0} = \lim_{K_s \to \infty} \frac{K + \frac{2}{3}BK'}{K - \frac{1}{3}BK'} = \lim_{K_s \to \infty} \frac{\left(1+\frac{2}{3}B\right)K_s + \left(2-\frac{2}{3}B\right)K_0}{\left(1-\frac{1}{3}B\right)K_s + \left(2+\frac{1}{3}B\right)K_0}$$

$$= \frac{1+\frac{2}{3}B}{1-\frac{1}{3}B} \simeq 1+B$$

$$\lim_{\substack{K_s \to \infty \\ \omega \to 0}} \frac{\sigma_e}{\sigma_0} = \lim_{K_s \to \infty} \frac{K + \frac{2}{3}BK'}{K - \frac{1}{3}BK'} \simeq 1+B$$

In summary, the imbedded sphere model with sphere concentration being small leads to a frequency dependent effective conductivity and effective dielectric constant. In addition, it shows that $\frac{K_e}{K_s} - 1$ and $\frac{\sigma_e}{\sigma_o} - 1$ are directly proportional to the volume of the impurity contained in the support medium.

Conclusions and Recommendations

The presence of impurities in a dielectric medium affect the frequency dependents of the dielectric constant and loss tangent. Curves showing this effect are presented in this chapter for various values of the parameters characterizing the sustaining medium and the dielectric impurities.

$\theta = \dfrac{K_s}{K_o} = 100$

$\phi = \dfrac{\sigma_s}{\sigma_o} = 10$

$\dfrac{K_e}{K_o} = 1$ for all other values of ϕ

$\dfrac{K_e}{K_o} = 1$ for $\theta = 10$

$\dfrac{K_e}{K_c}$

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$\theta = \dfrac{K_s}{K_o} = 10,000$

$\phi = \dfrac{\sigma_s}{\sigma_o} = 10$

$\dfrac{K_c}{K} = 1$ for all other values of ϕ

$\dfrac{K_c}{K_o} = 1$ for $\theta = 10$

K_e/K_o

13.5	$B = .06$
11.4	$B = .05$
9.35	$B = .04$
7.25	$B = .03$
5.16	$B = .02$
3.08	$B = .01$

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$$\phi = \frac{\sigma_s}{\sigma_o} = 10^3$$

$$\Theta = \frac{h_s}{K_o} = 10$$

$$\frac{\sigma_c}{\sigma_o} = 1 \quad \text{for } \phi = 10 \text{ and all } \Theta$$

$$\frac{\sigma_c}{\sigma_o} = 1 \quad \text{for all other values of } \Theta$$

B = .06   2.25

B = .05   2.05

B = .04   1.84

B = .03   1.63

B = .02   1.42

B = .01   1.21

122

B = .06   126

B = .05   105

B = .04   84

B = .03   64

B = .02   43

B = .01   22

$\phi = \dfrac{\sigma_s}{\sigma_o} = 10^5$

$\theta = \dfrac{k_s}{k_o} = 10$

$\dfrac{\sigma_c}{\sigma_o} = 1$ for $\phi = 10$ and $\theta = 10$

$\dfrac{\sigma_c}{\sigma_o} = 1$ for $\theta = 10^3$ and $\theta = 10^4$

$\dfrac{\sigma_c}{\sigma_o}$

$10^2 \quad 10^4 \quad 10^6 \quad 10^8 \quad 10^{10} \quad 10^{12} \quad 10^{14} \quad 10^{16} \quad 10^{18}$

1   10   30   50   70   90   110

$\phi = \dfrac{\sigma_s}{\sigma_o} = 10^5$

$\theta = \dfrac{K_s}{K_o} = 100$

$\dfrac{\sigma_e}{\sigma_o} = 1$ for $\phi = 10$ and all θ

$\dfrac{\sigma_e}{\sigma_o} = 1$ for $\theta = 10^3$ and $\theta = 10^4$

B = .06   2.74

B = .05   2.45

B = .04   2.16

B = .03   1.87

B = .02   1.58

B = .01   1.32

$\dfrac{\sigma_e}{\sigma_o}$

3

2

1

10^2 10^4 10^6 10^8 10^{10} 10^{12} 10^{14} 10^{16} 10^{18}

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$\dfrac{\sigma_e}{\sigma_o}$

10^5

10^4

10^3

10^2

10

1

$10^2 \quad 10^4 \quad 10^6 \quad 10^8 \quad 10^{10} \quad 10^{12} \quad 10^{14} \quad 10^{16} \quad 10^{18}$

ω

$\phi = \dfrac{\sigma_s}{\sigma_o} = 10^7$

$\theta = \dfrac{K_s}{K_o} = 10$

$\dfrac{\sigma_e}{\sigma_o} = 1 \quad \text{for } \phi = 10 \text{ and all } \theta$

$\dfrac{\sigma_e}{\sigma_o} = 1 \quad \text{for } \theta = 10^4$

$B=.06$
$B=.05$
$B=.04$
$B=.03$
$B=.02$
$B=.01$

1.25×10^4
1.84
$.83$
$.63$
$.42$
$.21$

125

$\frac{\sigma_e}{\sigma_o}$

200

160

120

80

40

1

$\phi = \frac{\sigma_s}{\sigma_o} = 10^7$

$\theta = \frac{K_s}{K_n} = 100$

$\frac{\sigma_e}{\sigma_o} = 1$ for $\phi = 10$ and all θ

$\frac{\sigma_e}{\sigma_o} = 1$ for $\theta = 10^4$

174

145

116

88

59

30

10^2 10^4 10^6 10^8 10^{10} 10^{12} 10^{14} 10^{16} 10^{18}

ω

126

$\phi = \dfrac{\sigma_s}{\sigma_o} = 10^7$

$\theta = \dfrac{k_s}{k_o} = 1000$

$\dfrac{\sigma_e}{\sigma_o} = 1$ for $\phi = 10$ and all θ

$\dfrac{\sigma_e}{\sigma_o} = 1$ for $\theta = 10^4$

127

$\phi = \dfrac{\sigma_s}{\sigma_o} = 10^9$

$\theta = \dfrac{K_s}{K_o} = 10$

$\dfrac{\sigma_e}{\sigma_o} = 1 \quad$ for $\phi = 10$ and all θ

1.25 × 10^6
1.04
.83
.63
.42
.21

B = .06
B = .05
B = .04
B = .03
B = .02
B = .01

$$\phi = \frac{\sigma_s}{\sigma_0} = 10^9$$

$$\theta = \frac{K_s}{K_0} = 100$$

$$\frac{\sigma_e}{\sigma_0} = 1 \quad \text{for } \phi = 10 \text{ and all } \theta$$

σ_e/σ_0

10^5 10^4 10^3 10^2 1

$1 \quad 10^2 \quad 10^4 \quad 10^6 \quad 10^8 \quad 10^{10} \quad 10^{12} \quad 10^{14} \quad 10^{16} \quad 10^{18}$

θ

B=.06
B=.05
B=.02
B=.01

1.73×10^4
1.44
1.15
.87
.58
.29

$\phi = \dfrac{\sigma_s}{\sigma_o} = 10^9$

$\theta = \dfrac{k_s}{k_o} = 10^3$

$\dfrac{\sigma_e}{\sigma_o} = 1$ for $\phi = 10$ and all θ

$\dfrac{\sigma_e}{\sigma_o}$

130

$$\phi = \frac{\sigma_s}{\sigma_o} = 10^9$$

$$\theta = \frac{K_s}{K_a} = 10^4$$

$$\frac{\sigma_e}{\sigma_o} = 1 \quad \text{for } \phi = 10 \text{ and all } \theta$$

σ_e/σ_o

3

2

1

131

10^2 10^4 10^6 10^8 10^{10} 10^{12} 10^{11} 10^{13} 10^{18}

B=.06   2.8

B=.05   2.5

B=.04   2.2

B=.03   1.9

B=.02   1.6

B=.01   1.3